VAPOR-LIQUID EQUILIBRIA OF A LOW GWP REFRIGERANT, R-1234ZE(E), MIXED WITH A POE LUBRICANT

BY

JESSICA BOCK

DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Mechanical Engineering
with a minor in College Teaching
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2015

Urbana, Illinois

Doctoral Committee:

Professor Anthony M. Jacobi, Chair
Professor M. Quinn Brewster
Professor Predrag Hrnjak
Professor Xinlei Wang

Abstract

Novel vapor-liquid-equilibria data (P-T-x) and liquid densities of binary mixtures of an emerging low-GWP (Global Warming Potential) refrigerant, R-1234ze(E), and a polyol ester (POE) oil, RL68H, are measured. Data are presented for oil mass fractions ranging from 0 to 0.85 over a temperature range from -10 to 60°C, and the results are compared to the properties of mixtures of R-134a with RL68H.

In addition to providing new pure-refrigerant and refrigerant/oil property data, a comparison of the performance of five mixture models is undertaken, namely: the Wilson model, NRTL, UNIQUAC, Heil, and Raoult's law. Overall, the Heil model provides the best agreement in pressure predictions for R-1234ze(E)/RL68H mixtures, with RMS deviations less than 0.5%, while NRTL RMS deviations are less than 1%. However, comparable performance was found for the much simpler Raoult's law, with increased deviations at the highest oil concentration. Model sensitivity and applicability of Raoult's law for refrigerant/oil mixtures in general are investigated.

The experimental data and modeling results presented are especially valuable for engineers working in the automotive air-conditioning and refrigeration industries. The refrigerant R-1234ze(E) is one of the leading alternatives for replacing R-134a and is a member of the HFO family of chemicals that includes other low-GWP refrigerants. Accurate models for the new refrigerants and refrigerant/oil mixtures are essential for designing and analyzing refrigeration and air-conditioning systems with reduced environmental impact.

Table of Contents

Nomenclature

Symbols

a	PR EOS parameter
A	PR EOS parameter
AAD	average absolute deviation [%]
b	PR EOS parameter
B	PR EOS parameter
m	mass fraction
M	mass [kg]
MW	molar mass [kg/kmol]
g	Gibbs energy [kJ/kmol]
OBJ	objective function
P	pressure [kPa]
Pe	Poynting effect
q	UNIQUAC parameter
r	UNIQUAC parameter
R	gas constant [kJ/kmol-K]
RMS	root mean square error [%]
T	temperature [K]
v	specific volume [m^3/kg]
$\bar{v}$	molar specific volume [m^3/kmol]
V	volume [m^3]
x	liquid mole fraction
y	vapor mole fraction
Z	compressibility factor

Superscripts

c	combinatorial
E	excess
r	residual

Greek Symbols

α	PR EOS parameter
α_{ii}	NRTL parameter
γ	activity coefficient
θ	UNIQUAC parameter
Θ	arbitrary parameter
κ	PR EOS parameter
λ	binary interaction parameter
Λ	mixture model parameter
ρ	density [kg/m^3]
τ	mixture model parameter
φ	UNIQUAC parameter
Φ	fugacity coefficient
ω	acentric factor

Subscripts

1	component 1
2	component 2
c	critical
cal	calculated value
exp	experimental data
liq	liquid phase
o	oil
r	refrigerant
sat	saturation
tot	total
u	universal
vap	vapor phase

Chapter 1 – Background and Objectives

1.1 Introduction

Following the 1987 Montreal Protocol, the air conditioning and refrigeration industry began phasing out chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants due to their high ozone depletion potentials. Global warming concerns led to the 1997 Kyoto Protocol targeting hydrofluorocarbons (HFCs), along with the mobile air-conditioning MAC-directive [1] and F-gas regulation placing limits on the global warming potential (GWP) of fluids used in automotive applications. In refrigeration and air-conditioning applications HFCs are widely used, including R-134a which is used in wide variety of HVAC&R applications, including automobile air conditioning. Refrigerant R-134a has a GWP of roughly 1400 [2].

As of 2010, more than 99% of all new automobiles were equipped with an air-conditioning system [3]. With over 65 million vehicles produced in the US in 2013 [4], the phase out of R-134a will clearly have a major impact on the automobile industry. Drop-in replacements are appealing to automobile manufacturers due to potential cost-savings. Two of the leading drop-in alternatives with thermodynamic properties similar to those of R-134a are R-1234yf and R-1234ze(E) [5]. Both refrigerants are hydrofluoroolefins (HFOs) and have GWPs less than 6 [2].

Nearly all vapor-compression systems require a compressor lubricant, and the lubricant concentration varies from system to system, throughout the system, and throughout the duty cycle of the system. The presence of lubricant oil in refrigerants can have a significant effect on thermodynamic and transport properties including saturation pressure and viscosity; the presence of the lubricant can have a significant effect on system performance [6]. It is therefore important to consider the properties of refrigerant and oil mixtures in the design of vapor compression refrigeration and air-conditioning systems.

The emergence of a 4th generation of refrigerants necessitates the investigation of new refrigerant and oil mixture properties. Considerable experimental efforts are underway to ascertain system performance using alternative refrigerants [7-11]. Accurate mixture models can reduce the amount of experimental data required to represent and predict thermophysical properties. Prior research has been conducted on refrigerant and oil mixtures and has demonstrated the success and utility of mixture models. The current study is aimed at extending the available thermophysical property database for HFO refrigerants and identifying or developing mixture models to accurately represent the thermophysical property data of these refrigerants mixed with lubricating oils.

1.2 Literature Review

1.2.1 Thermophysical Properties of Pure R-1234ze(E)

Recently, a significant amount of research has been conducted regarding the classification of the low-GWP refrigerant replacement candidates. Having properties similar to R-134a, R-1234ze(E) has garnered attention as a potential drop-in replacement. In 2009, Grebenkov *et al.* [12] presented vapor pressure data and an equation of state based on the extended corresponding states (ECS) model. Scatter in the data led to large deviations from the model, necessitating further measurements for an accurate thermodynamic description. Brown *et al.* (2010) [13] applied group contribution methods and the Peng-Robinson EOS to predict thermodynamic properties of eight fluorinated olefins, including R1234ze(E), using only the normal boiling point (NBP), temperature, and molecular structure. Limited experimental data were available for comparison, but the approach showed good agreement when compared to data for R-134a and R-1234yf. Experimental data for thermophysical properties have since been reported for temperatures ranging from 205 to 430 K and pressures up to 95 MPa [12, 14-21]. Experimental data for thermal conductivity and liquid viscosity are considerably scarcer [22, 23]. Brown *et al.* (2014) [24] provided a review of thermophysical property measurements of R-1234ze(E) and compared the experimental data to the previously mentioned predictive method using only the NBP and molecular structure; estimated values agreed with the measurements to within 5% for seven properties.

As new data were presented for the pure refrigerant R1234ze(E), researchers pursued a more accurate equation of state (EOS). In 2010, Akasaka [25] presented a new thermodynamic model for 1234ze(E) based on the extended corresponding states principle, and it compared well to available experimental data—within 0.5% for saturations pressure and 0.2% agreement with saturated liquid density data. McLinden *et al.* [19] provided comprehensive P-ρ-T measurements for pressures up to 15 MPa over the temperature range of 240 to 420 K. They developed an EOS in terms of the Helmholtz energy that was accurate for the currently available data but required additional property measurements for further improvement. Akasaka [26] presented a Helmholtz-explicit EOS for R-1234ze(E) with good predictive performance for pressures up to 15 MPa and temperatures from 240 to 430K. No numerical values for uncertainty were provided for the new EOS. REFPROP v9.0 [27] employs the equation of state developed by Akasaka [26] and an established model for estimating thermal conductivity and viscosity [28, 29].

Molecular simulations using a force field model have also provided reliable predictions of saturation pressures of R-1234ze(E) and refrigerant blends containing R-1234ze(E) [30, 31]. However, molecular models require extensive knowledge of the fluid and comprehensive thermophysical descriptions of commercial lubricant oils are generally unavailable, making it difficult to apply molecular simulations to refrigerant/oil mixtures, which will be discussed in the next section. The Peng-Robinson EOS (PR-EOS) has been shown to accurately describe R-1234ze(E) [24, 32] and has a convenient form for system analysis and mixture modeling.

1.2.2 Refrigerant/Oil Mixture Data

While pure refrigerant data for R-1234ze(E) are available in the open literature, data for binary mixtures of HFO refrigerants and oil are scant. A 2002 review by Marsh and Kandil [33] summarizes experimental investigations of HFC refrigerants, such as R-134a and R32, with synthetic lubricant oils. The authors describe the performance behavior and provide chemical structure diagrams of four categories of synthetic lubricants, including polyol esters (POE). The results of 26 experimental studies for refrigerant/oil properties are included in the review. Only a few studies reported property measurements beyond P-T-x data. The authors note the difficulty for generalization due to the lack of information about pure lubricant properties.

Numerous publications are available for refrigerant/lubricant mixtures containing other refrigerants [34-44]. Marcelino Neto & Barbosa [40] cited 21 additional studies on phase equilibria and thermophysical properties of mixtures of halocarbon refrigerants and lubricating oils. The authors presented solubility, liquid phase density, and viscosity data for the binary mixture of R-600a + POE ISO 7 for temperatures ranging from 10 to 60°C. The PR-EOS and Heil [45] activity coefficient model provided good agreement for density, pressure, and solubility, giving an RMS deviation of 0.77% for saturation pressure.

Grebner & Crawford [41] provided VLE measurements for R-12 + mineral oil and R-134a + synthetic oil for temperatures from -46 to 121°C with oil mass fractions ranging from 0 to 0.95. The authors developed a 7-term empirical model that described the mixture behavior more accurately than other theoretical methods such as Flory-Huggins.

Martz & Jacobi [38] and Burton & Jacobi [39] studied a total of six refrigerants with POE oils over a range of concentrations and compared the results with six activity coefficient mixture models. The results showed consistently poor agreement with the UNIQUAC model. Martz & Jacobi provided tabulated values for pressure, temperature, liquid density and mass fraction for refrigerant mass fractions from 0.2 to 1 over the temperature range -20 to 80 °C. Burton & Jacobi provided tabulated values for the same properties plus refrigerant mole fraction for temperatures from 10 to 50 °C for R32/POE and -45 to 45 °C for R-410A/POE. Martz & Jacobi also provided a temperature dependent correlation for liquid density of the POE oil RL68H used in both studies

Xu *et al.* [37] and Han *et al.* [42] measured VLE data for refrigerant mass fractions ranging from 0.1 to 0.95 for R-161 and two different POE lubricants; temperatures included 10 to 70°C. Tabulated values for pressure, temperature, and refrigerant mass fraction were provided. An average relative pressure deviation of less than 2% was reported for results from the non-random two-liquid theory (NRTL).

Property measurements for HFO-refrigerant and lubricant mixtures are scarce. In the past year, limited VLE studies have been published from two research groups for R-1234yf and R-1234ze(E) with synthetic lubricants [46-49]. *P-T-x* data were reported for a range of oil concentrations for temperatures from 10 to 80 °C. Density measurements were not included in any study. Complete miscibility was observed for the mixtures, and the HFO refrigerants exhibited greater solubility than R-134a. A 2014 study by Bobbo *et al.* [50] investigated the solubility of R-1234yf in two commercial PAG oils; regions of partial immiscibility were present, indicating potential performance issues of HFO-refrigerants mixed with PAG oils.

1.2.3 Modeling Refrigerant/Oil Mixtures

Mixture models are used to predict mixture properties at given thermodynamic conditions. Good models can aid in the design and analysis of refrigeration and air-conditioning systems and reduce the need for extensive experimental data. Various models exist for VLE predictions, including EOS models, activity-coefficient models, empirical models, molecular models, and EOS models combined with excess free energy (or liquid activity coefficient), EOS-G^{ex} models. According to a review by Islam & Rahman [51], the models most frequently used in VLE calculations are Redlich-Kister, Wilson, Margules, NRTL, UNIQUAC, Van Laar, and UNIFAC. Among these, the Wilson, NRTL, and UNIQUAC (Universal Quasi-Chemical) methods are the most widely and successfully used [52].

In previous studies, refrigerant/oil mixtures have been compared to various models. Tesser *et al.* [34-36] found good results with the Flory-Huggins model and PR-EOS but did not compare with activity coefficient models. The binary mixtures included perfluoropolyether lubricant Fluorolink ® D10H paired with R-125, R-134a, R-143a, and R-32. Temperatures ranged from -10 to 50°C.

Elvassore & Bertucco [43] found that a cubic equation of state with group contributions had better agreement with data for R-134a +hexadecane than did the Flory-Huggins, Wilson, Heil, NRTL, UNIQUAC and Redlich-Kister methods. The method also showed good agreement with other HFC +POE data from the literature. Bertucco *et al.* [44] reported good agreement for a modified-perturbed-hard-sphere-chain EOS for refrigerant and oil mixtures. These EOS models were compared to limited data and needed further investigation to confirm accuracy for a range of mixtures. Results from the Heil method combined with the PR-EOS were more accurate than Flory-Huggins theory for R-600a+POE [40].

Correlations for estimating the thermophysical properties of refrigerant/lubricant solutions were reviewed by Conde (1995) [53]. Simplified equations were provided for estimating pure lubricant properties as well as refrigerant/oil properties. The review provided some comments regarding validity of the correlations presented, but was not rigorous or quantitative.

The Heil and Wilson methods performed similarly for the refrigerant/oil mixtures investigated by Martz & Jacobi, and were more accurate than two modified Wilson methods and NRTL; UNIQUAC [38] produced unacceptable results in all cases. In a similar study, mixtures of POE with R-32, R-125, and R-410A were investigated over a range of refrigerant mass fractions from 0.2 to 0.95. Again the Heil model performed well and UNIQUAC performed poorly. Results for the R-410A mixture were inconclusive due to inaccurate vapor composition measurements [39]. In both studies the models were fitted in terms of pressure and evaluated based on 2σ errors for predicted pressure.

Xu *et al.* [37] determined that NRTL produced accurate results for HFC-161 +POE (Planetelf ACD 32) and was more convenient than complicated EOS models such as PC-SAFT (perturbed-chain statistical associating fluid theory). The NRTL model was correlated with experimental data over the temperature range 283.15 to 343.15 K for refrigerant mass fractions ranging from 0.1-0.95. The model was fitted using an objective function based on experimental and predicted activity coefficients; an average relative deviation (ARD) and maximum relative deviation of 1.94% and 5.71% were reported for the predicted pressures.

Dong *et al.* [32] reported accurate correlations for the refrigerant blend R-1234ze(E)+R-600a using the NRTL method and PR-EOS. Pressure data were reported for the limited temperature range of 258 to 288 K. The model was fitted using pressure, and the maximum absolute relative deviation of predicted pressure was 0.32%.

Youbi-Idrissi and Bonjour (2008) [6] reviewed refrigerant/oil related research and provide a thorough description of impacts the lubricant has on a refrigeration system. The authors also briefly describe different mixture modeling approaches and associated challenges. The approaches include empirical correlations, local composition models, cubic equations of state, group contribution methods, perturbed hard sphere chain method (PHSC), and statistical associating fluid theory (SAFT). Tabulated deviations associated with predicted pressures for multiple refrigerant/lubricant mixtures from five different studies were also presented, indicating superior performance from the Heil model in the majority of cases.

In 2009, Restrepo [54] compared the performance of six mixture models for three refrigerant/oil mixtures—R-134a/POE 220, R-22/AB 150, and R-22/AB 300. The study did not mention error or deviation, but asserted that the Wohl 3-suffix equations provided satisfactory results when compared with the Wilson, Heil, NRTL, T-K, and UNIFAC models.

A review of activity coefficient methods by Islam [51] discussed reported performances of several activity coefficient models including the Wilson, NRTL, and UNIQUAC methods. The review included a discussion of functional forms of the objective function used to fit binary interaction parameters of the mixture models. The focus of the review was refrigerant blends rather than refrigerant/oil mixtures.

Marcelino Neto and coworkers [55] proposed a departure-function approach for calculating thermodynamic properties of refrigerant/lubricant mixtures. Properties for the binary mixtures R-600a/AB 5 and R-600a/POE 7 are predicted using the approach with the Peng-Robinson equation of state. The study did not provide quantitative data describing the accuracy of the predictions.

In one of the few studies of an HFO refrigerant mixed with a lubricant, Marcelino Neto & Barbosa [46] investigated the absorption of R-1234yf in POE ISO VG 10 and compared the results with R-134a/POE ISO VG 10 behavior. The authors reported mixture pressures for refrigerant mass fractions from 0.15 to 0.9 over the temperature range 13 to 80 °C. The pressure data were used to determine the binary interaction parameter for a Peng-Robinson equation of state combined with a quadratic mixing rule. The authors reported remarkably good agreement in pressure predictions for Raoult’s law and a slight improvement employing the cubic equation model. The maximum AAD and RMS values were 6.43 and 1.31 %, respectively for Raoult’s law.

The very recent studies by Sun *et al.* [47, 48] present excellent agreement in pressure predictions using the Wilson and NRTL models for mixtures with R-1234ze(E) and POE lubricants. Absolute average deviations in pressure predictions were less than 1%. Modeling efforts were limited to a single method in each publication. The authors switched from the NRTL model [47] to the Wilson model [48] with no explanation for the change or comparison of model performance.

Other mixture modeling efforts have been reported, including purely predictive modeling techniques and studies of high-pressure systems using R-744 [50, 56-60].

1.2.4 Summary

Various models have been reported as describing mixture behavior more reliably for different refrigerant/lubricant components in the available literature, so it is important to check the accuracy of multiple models in order to find the best fit. Often, only one or two modeling methods are evaluated in a given study. The lack of comparison amongst multiple models for a given mixture makes it difficult to draw conclusions regarding the generality of model performance for refrigerant/lubricant mixtures. Lack of property information and approximated molar masses for the pure lubricants further hinders the quest for generality; molar mass is required when converting reported refrigerant mass fraction to mole fraction for evaluating the models

Additionally, mixture model evaluations are not always reported in terms of the same parameters. Including statistical parameters for average absolute deviation (AAD), root mean square (RMS) error, and bias would provide a clearer description of the model performance. Including a single performance evaluation criterion, such as 2-σ (95% CI) error, can be misleading if deviations of the predicted values are large. It would also be useful for studies to provide performance results for multiple properties so that researchers can determine if a model can accurately predict one property while failing to predict another.

The current study compares the Wilson [62], NRTL [63], UNIQUAC [64], and Heil [45] models using the PR-EOS [65] with experimental data for mixtures of R-1234ze(E) with RL68H. Agreement with Raoult's law is also investigated. Side-by-side comparisons of model performance for R-134a/POE and R-1234ze(E)/POE are used to make limited conclusions about model sensitivity and model applicability for R-1234ze(E).

1.3 Objectives

1.3.1 Needed Research

It is evident from the literature review that thermodynamic data of refrigerant/lubricant mixtures are valuable. Researchers can utilize the information to design, simulate and analyze HVAC&R systems and components. As current refrigerants are being phased out in lieu of more environmentally friendly alternatives, it is imperative that researchers and designers stay abreast of the emerging alternative refrigerants and associated thermophysical descriptions.

Accurate descriptions are especially needed for emerging refrigerants, including R-1234ze(E) from the hydrofluoroolefin (HFO) family of chemicals, as international agreements and regulations lead to the discontinued production of systems using R-134a. Researchers are actively working on characterizing these pure refrigerants and developing suitable equations of state. New thermophysical data can lead to more accurate equations of state.

Highly accurate equations of state for the pure refrigerants, unfortunately, do not describe the fluids used in application. Typical vapor compression cycles used in air-conditioning and refrigeration systems require the addition of a lubricant, which will affect the fluid properties and thus system performance. The dearth of literature available on binary mixtures of HFOs and lubricants signifies a clear need for additional research in this area.

The three most frequently used models for describing the VLE behavior of binary mixtures (Wilson, NRTL, and UNIQUAC) were proposed more than 30 years ago. The fact that these models remain the most widely used suggests the difficulty associated with developing a significantly more accurate model while maintaining computational convenience. The new hydrofluoroolefin (HFO) family of refrigerants may lend themselves to a new or modified mixture modeling method. The data gleaned from the proposed research will be used to determine if existing mixture models can satisfactorily describe the VLE behavior of the new HFO- refrigerant, R-1234ze(E), mixed with a polyol ester (POE) lubricant. The study also expands the refrigerant/oil database, potentially allowing conclusions to be drawn regarding modeling of refrigerant/oil mixtures in general.

1.3.2. Statement of Objectives

The objectives of the current research are as follows:

1. Obtain VLE (P-ρ-T) data for the pure refrigerant R-1234ze(E) over the temperature range -10 to 60°C.

2. Obtain VLE (P-ρ-T-x) data for the mixture of R-1234ze(E) and the refrigerant lubricant RL68H over the temperature range -10 to 60°C with oil-mass fractions ranging from 0 to 0.8.
3. Develop semi-theoretical activity-fugacity (γ-ϕ) models of VLE behavior for the mixture studied and evaluate the accuracy of existing mixture models (i.e. Wilson method, UNIQUAC, NRTL, Heil).
4. Recommend an EOS and mixture model for the R-1234ze(E)/RL68H mixture based on experimental data.
5. Investigate mixture model performance for refrigerant/lubricant mixtures in general, and for this specific family of chemicals.

Chapter 2 – Experimentation

2.1 Apparatus

Experiments were conducted in a closed system consisting of a pressure vessel and a circulation loop. A schematic of the apparatus is provided in Figure 1. The system is heated and cooled via internal and external coils connected to a chiller with a large reservoir tank, through which an ethylene glycol/water mixture (50% by volume) is circulated at a constant temperature, maintained by a PID controller.

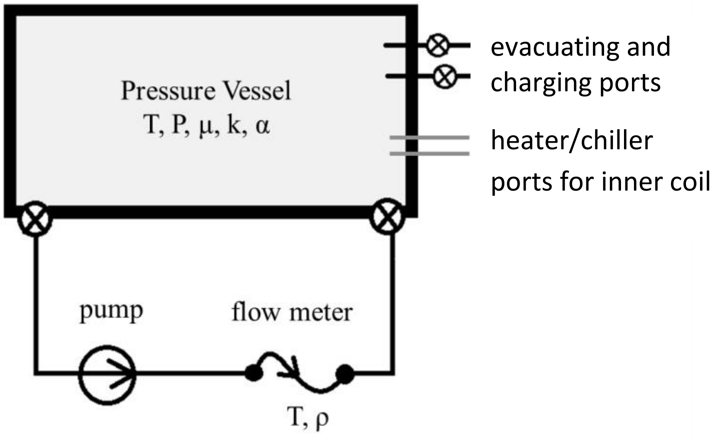


Figure 1: Schematic of experimental apparatus.

A circulation loop, consisting of a gear pump (Micropump model VD56T34F5301J) and a Coriolis-effect flow meter (MircoMotion model CMF025M313NQBAEZZZ) are connected to liquid ports on the pressure vessel with 3/8 in (9.52 mm) OD copper tubing. The density is determined from the resonant frequency of the vibrating tube in the flow meter. The flow meter is also equipped a Pt100 RTD for measuring temperature. The pump motor is controlled with a variable-frequency drive (TECO JNEV-1P5-H1), which allows adjustments to the mass flow rate to ensure a single-phase fluid in the flow meter for accurate liquid density measurements.

A pressure vessel made of SS316Ti alloy (Berghof, Inc.) is outfitted with two borosilicate glass windows for visual access and a magnetically driven stirrer with two sets of paddle wheels for thorough mixing. A pressure gauge, pressure transducer (tecsis P3290B080022), rupture disc, and thermocouple well with a K-type probe were incorporated in the pressure vessel design. There are two threaded ports with O-ring fittings for a viscometer and thermal conductivity sensor, both with PT100RTDs. A detailed schematic of the stainless steel pressure vessel is shown in Figure 2. The pressure vessel has custom-designed 28 mm thick Teflon insulation jacket. Additionally, during experiments the entire apparatus was enclosed in more than 6cm of soft Buna-N/PVC foam thermal insulation to reduce heat exchange with the surroundings.

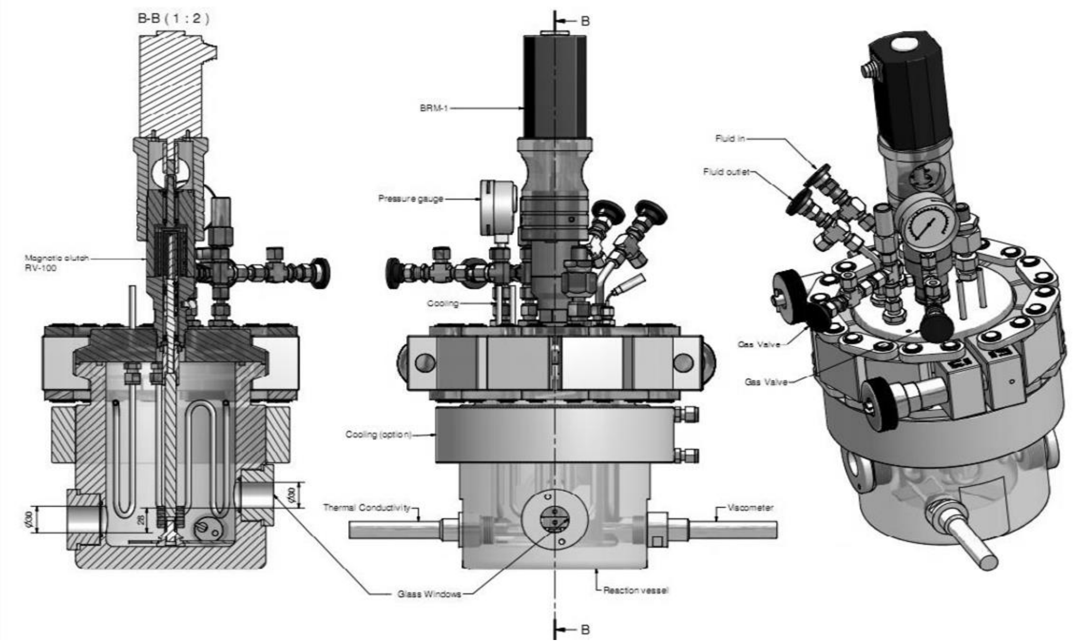


Figure 2: Detailed schematic of pressure vessel and instrumentation, *courtesy of Berghof, Inc*.

A National Instruments NI 9208 data acquisition card, NI cDAQ-9171 chassis, and custom LabVIEW program were used for data acquisition from the pressure transducer and flow meter. The pressure vessel and instrumentation have the capability of operating over temperatures from -30 to 150°C and pressures up to 15 MPa. The flow meter, however, is limited to pressures below 1730 kPa.

2.2 Procedure

The lid of the pressure vessel was removed to charge the system with lubricant. The charge mass of the lubricant was determined from the change in mass of the lubricant sample container. The lid to the oil container and the pressure vessel were closed quickly to minimize exposure to the atmosphere.

After replacing pressure vessel lid and prior to charging the system with refrigerant, the apparatus was evacuated with a vacuum pump (FJC Air Conditioning Products model VP3.0). During evacuation, the system was isolated from the environment but all internal valves were open to allow complete evacuation. The refrigerant tank was connected to the charging port via a refrigerant charging hose and placed on a scale to monitor the charge mass. Starting from the mixture with the largest oil concentration, the system was charged with refrigerant and the liquid-vapor interface was observed using the sight glass windows on the pressure vessel. Additional refrigerant was added to the system for the subsequent experiments until data for the desired range of oil concentration ratios were obtained.

The system was charged with dry nitrogen before and after collecting data to ensure no leaks were present. Leak tests were conducted at 1725 kPa, requiring pressure fluctuations to be within the measurement uncertainty for more than 24 hours.

After the system was charged the pump was turned on to begin circulating the fluid. The heating/cooling system was set to the desired temperature and the system was monitored until steady-state conditions prevailed. Steady state conditions are reached when 95% of the temperature, pressure, and density fluctuations are within the uncertainty (95% CI) of the measurements for more than five minutes. The values reported for temperature, pressure, and density are averaged from 90+ data points, with a sampling rate of 1.5 Hz. The reported measurement values are obtained by averaging for sampling periods of at least one minute within the period of steady state, such that experimental conditions maintain steady state before and after sampling.

The increased viscosity of the mixture with the highest oil makes obtaining accurate liquid density values more difficult. The mixture with an overall refrigerant mass fraction of 0.2 exhibited less steady behavior manifested as cavitation in the circulation loop where density is measured. In the cases where cavitation prevented longer durations of steady density measurements, reported values are averages of at least 40 measurements. This sample size is sufficient to assume a normal distribution of the data and avoid the use of the Student's t-distribution.

The total volume of the system was measured using both dry nitrogen and carbon dioxide. The compressed gas was transferred to a sample cylinder later used for refrigerants in the experiments. The mass of the sample cylinder was measured before and after charging the apparatus. After allowing time for the system to reach equilibrium, the temperature and pressure were recorded. Using the thermophysical property database available in Engineering Equation Solver EES*(1)* to evaluate vapor density, and substituting into the definition for density, the total volume of the system was determined to be 3.43 ± 0.01 L.

The overall refrigerant mass fraction, m_r, of the mixture is directly calculated from the charge masses, *M*, of the mixture components.

$$\left(m_r\right)_{mix} = \frac{M_r}{M_r + M_o} \tag{1}$$

The overall refrigerant concentration remains constant until the charge mass of a component changes. The liquid refrigerant concentration, however, changes with temperature. The liquid refrigerant concentration is determined using density, volume, and charge mass information, as described below.

The volume of the experiment apparatus can be dividing into a vapor and liquid phase, where the sum of the vapor and liquid volumes are equal to the total volume. The volume of the solution (liquid volume) can be expressed as

$$V_{liq} = \frac{M_{r(liq)} + M_o}{\rho_{liq}} \tag{2}$$

where $M_{r(liq)}$ is the mass of refrigerant in the liquid phase, ρ_{liq} is the measured liquid density, and m_o is the charge mass of the oil. Based on the significant difference in

---

(1) S.A. Klein, Engineering Equation Solver (EES) ©, Version 9.699, F-chart Software, Madison, Wisconsin, 2014.

saturation pressures of refrigerants and lubricants, the oil is assumed to exist only in liquid phase [69]. The mass of the refrigerant in the system is equal to the sum of the refrigerant mass in the liquid and vapor phases.

$$M_{r(liq)} + M_{r(vap)} = M_r \tag{3}$$

The mass of refrigerant in the vapor phase is

$$M_{r(vap)} = \left(V - V_{liq}\right)\rho_{r(vap)} \tag{4}$$

where V is the total volume of the system and $\rho_{r(vap)}$ is the vapor density of the refrigerant at system temperature, which can be found using an accurate equation of state. The vapor density of the pure refrigerant can be used for the mixture, assuming that no lubricant is present in the vapor phase. The fluid property database available in EES is used to evaluate the pure-refrigerant vapor density at system temperature and pressure; density values for R-1234ze(E) are obtained from the equation of state developed by Akasaka (2011) [26].

The refrigerant concentration in the liquid phase can be calculated on a mass and molar basis. The mass fraction of the refrigerant in the solution is

$$m_r = \frac{M_{r(liq)}}{M_{r(liq)} + M_o} \tag{5}$$

The mole fraction is determined using Eq. (6).

$$x_r = \frac{\dfrac{M_{r(liq)}}{MW_r}}{\dfrac{M_{r(liq)}}{MW_r} + \dfrac{M_o}{MW_o}} \tag{6}$$

where the molar mass of the refrigerant R-1234ze(E) is 114 kg/kmol and the molar mass of the lubricant RL68H is 765 kg/kmol. The presentations in the following chapters provide property data in terms of the mass fraction of refrigerant in the solution, unless otherwise noted.

2.3 Uncertainty

Measurement uncertainties are listed in Table 1.

Table 1: Measurement Uncertainties

Measurement	**Instrument Range/Uncertainty**	**Experimental Range**
Pressure	0 to 3447 kPa ±1.72 kPa	135 to 1725 kPa
Temperature	-30°C to 150°C ±0.04 K	-10 to 60°C
Liquid Density	±0.0005 kg/m^3	940 to 1270 kg/m^3
Concentration	Calculate from mass and density	0 to 0.8
Vapor Density	Determine from EOS	10 to 110 kg/m^3

Chapter 3 – Results & Discussion

R-134a (1,1,1,2-tetrafluoroethane) is a member of the HFC refrigerant family and has a simpler molecular structure than the proposed replacement R-1234ze(E) (*trans*-1,3,3,3-tetrafluoropropene), a hydrofluorinated olefin (HFO) refrigerant. The molecular structures of the two refrigerants are illustrated in Figure 3, reproduced from Raabe [30], where green spheres represents fluorine, gray represents carbon, and white represents hydrogen atoms. R-1234ze(E) has an additional carbon atom, and a carbon=carbon double bond. The molar mass of R-134a and R-1234ze(E) are 102 kg/kmol and 114 kg/kmol, respectively.

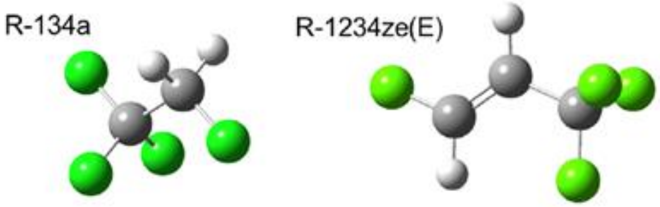


Figure 3: Molecules of R-134a, R-1234ze(E), and CO2 (reproduced from Raabe [30])

R-1234ze(E) is an attractive replacement for R-134a because it exhibits similar thermodynamic behavior but has a much lower global warming potential ($GWP_{R\text{-}134a} \approx 1400$ and $GWP_{R\text{-}1234ze(E)} \approx 6$). Further investigation of the alternative refrigerant will reveal if the difference in molecular structure significantly influences mixture behavior.

3.1 Pure Refrigerant Data

3.1.1 R-134a

Prior to measuring the thermophysical properties of the emerging refrigerant, R-1234ze(E), experiments were conducted using commercial grade R-134a. Property data for R-134a were used to troubleshoot and validate the experiment apparatus and method. The measured property values for the refrigerant agreed well with an accurate and widely accepted equation of state for the fluid developed by Tillner-Roth and Baehr [77]. Saturated pressure measurements agreed with values predicted by the EOS with an average error less than 0.1%. Saturated liquid density measurements agreed with predicted values from the equation of state with an average error of 0.11%.

3.1.2 R-1234ze(E)

Vapor-liquid equilibrium data for pure R-1234ze(E) are reported in this section. Averaged experimental results for saturation pressure are shown in Figure 4 as a function of temperature. The data agree well with predicted values from the equation of state presented by Akasaka (2011) [26], having a root mean square (RMS) error less than 0.09% and average absolute deviation (AAD) less than 0.6%.

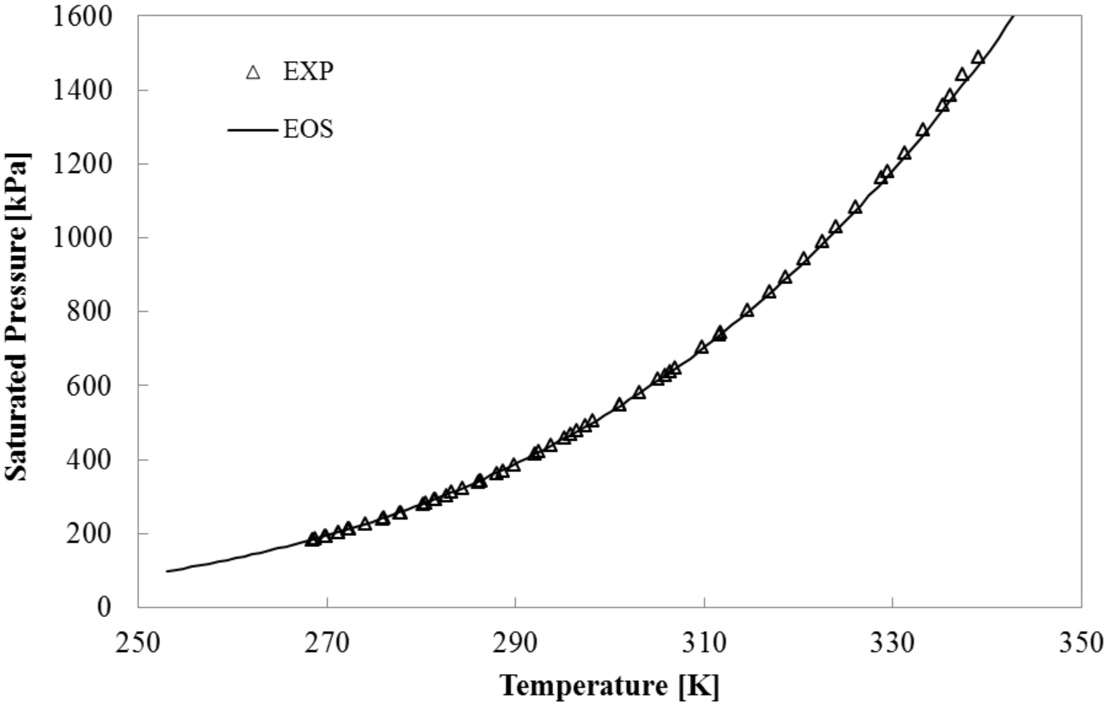


Figure 4: *R-1234ze(E) saturation pressure measurements compared to equation of state [26] predictions*

As seen in Figure 5, the experimental data for liquid density near the saturation line also agree well with predictions from the equation of state provided by Akasaka (2011) [26]. The predicted values shown in the plot represent the saturated liquid density of R-1234ze(E). The experimental data are near saturation but not exactly at saturation, due to the necessity for liquid-only flow in the Coriolis-effect flow meter. Cavitation or vapor flow would result in unreliable density measurements. This difference notwithstanding, the root mean square (RMS) error for liquid density is less than 0.02% and the average absolute deviation (AAD) is less than 0.2%.

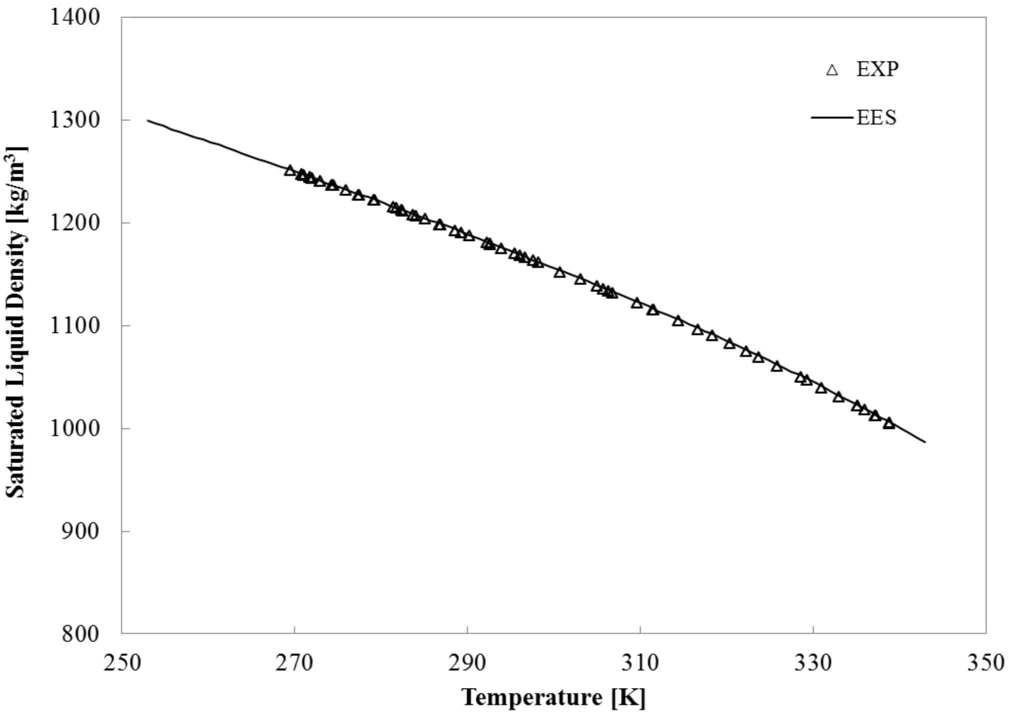


Figure 5: *R-1234ze(E) saturation liquid density measurements compared to equation of state [26] predictions*

3.2 Binary Mixture Data

Due to the presence of a compressor, vapor-compression cycles commonly require the addition of a lubricant. A variety of refrigerant lubricants are commercially available, and selection is based on compressor specifications.

Various commercially available lubricants have been, and continue to be, investigated for material compatibility with the new family of HFO refrigerants [10, 50, and 66]. R-1234yf has undergone more extensive testing with lubricants than has R-1234ze(E).

Immiscibility and partial miscibility are a concern for some lubricants. Polyol ester oils have been successfully paired with HFOs. R-1234ze(E) is more soluble than R-134a [66], indicating that higher viscosity lubricants may be favorable in order to maintain adequate bearing lubrication in the compressor. The commercially available polyol ester oil Emkarate ® RL68H was selected for this study.

RL68H is a refrigerant lubricant designed for high lubricity and is compatible with various refrigerants and compressor designs. RL68H was developed for use with HFC refrigerants, like R-134a, as well as CFCs, HCFCs, and blends. According to the manufacturer, RL68H can be used with reciprocating, centrifugal, rotary, screw, and scroll compressors.

VLE data reported for the binary mixture R-134a/RL68H in an earlier study [38] provide a basis for evaluating R-1234ze(E) as a drop-in replacement for R-134a. The saturation pressure and saturated liquid density of theR-134a/RL68H mixture are shown in Figures 6 and 7, respectively.

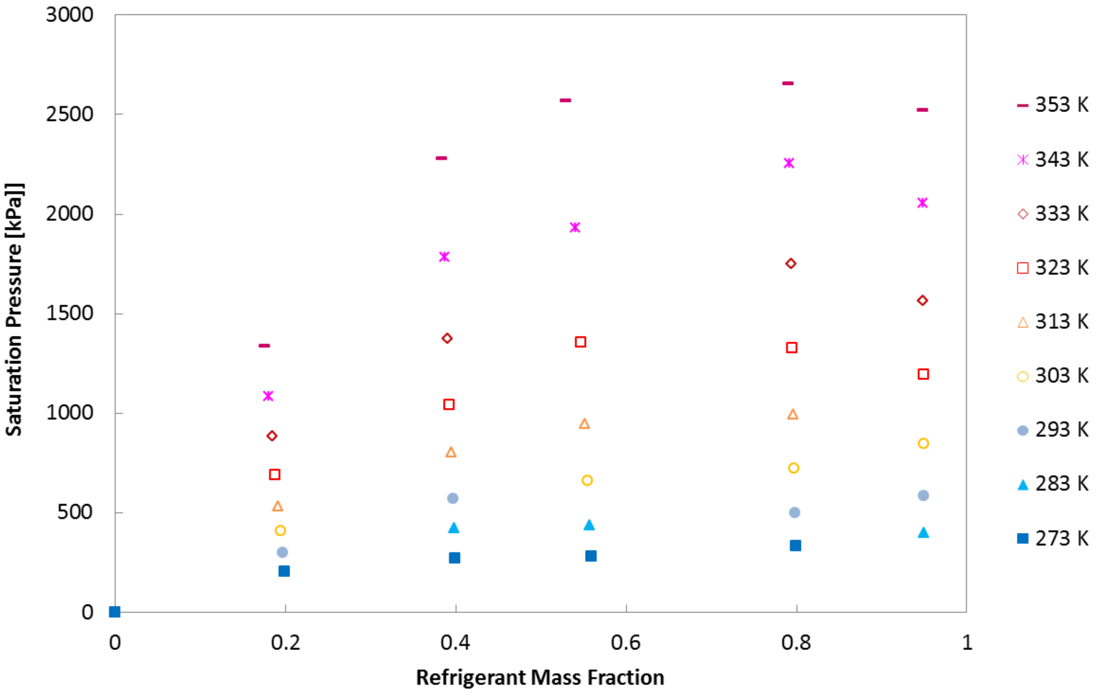


Figure 6: P-T-x data for R-134a/RL68H [reproduced from Ref 38]

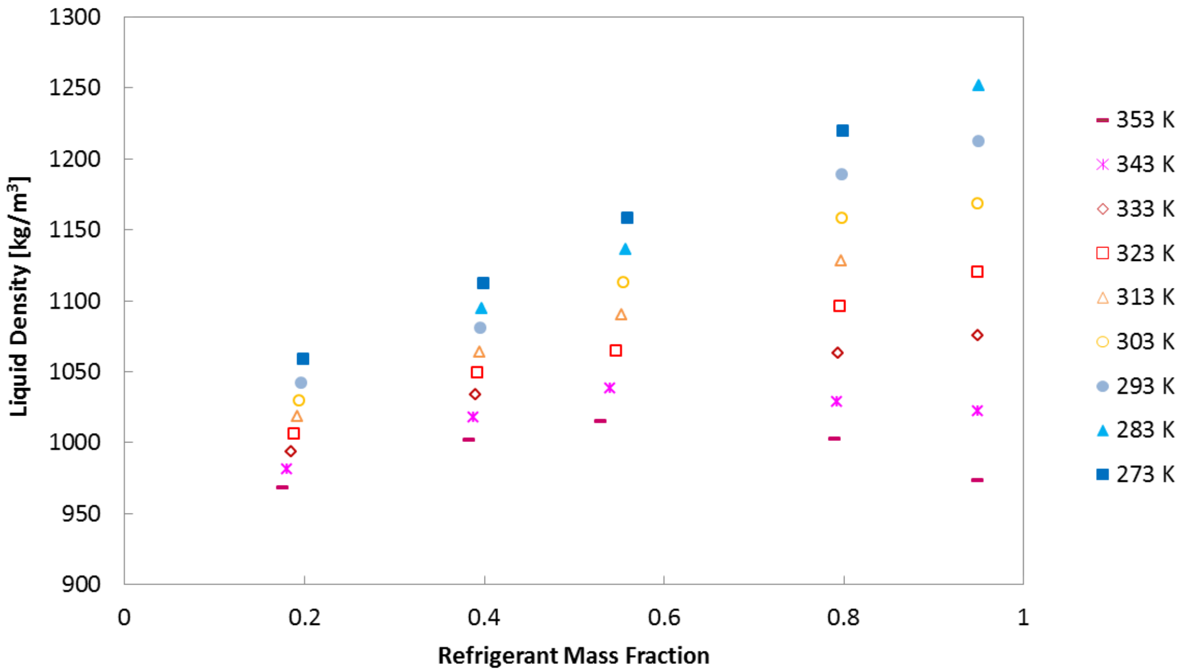


Figure 7: ρ-T-x data for R-134a/RL68H [reproduced from Ref 38]

Experimental P-T-x-ρ data for the mixture R-1234ze(E)/RL68H were obtained in the present study for temperatures from -5 to 60 °C. Refrigerant mass fractions of the liquid phase of the mixture ranged from 0.1 to 1.0. Saturation properties for the oil (x=0) were taken from the open literature [67]. The liquid density of the oil was calculated using a temperature-dependent curve-fit provided by Martz [38] for RL68H.

Saturated pressure data for the mixtures are presented in Figure 8 as a function of temperature and mass fraction of refrigerant in the liquid phase. Similarly, liquid density measurements are provided in Figure 9.

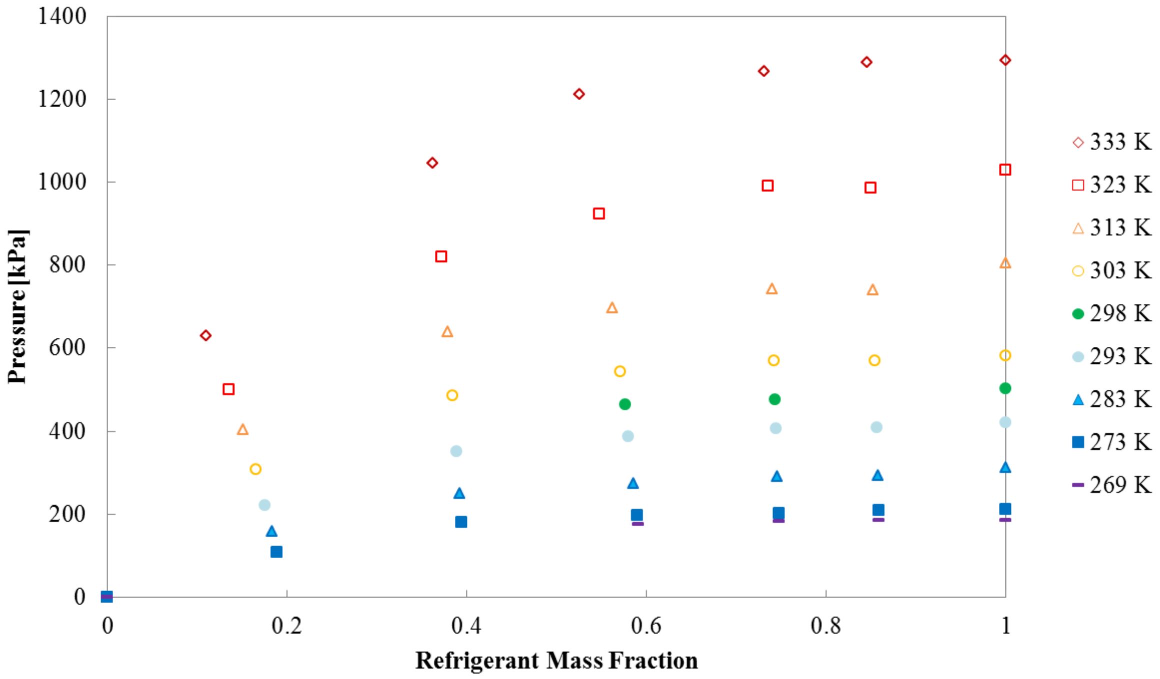


Figure 8: Saturation pressure as a function of temperature for R-1234ze(E)/RL68H

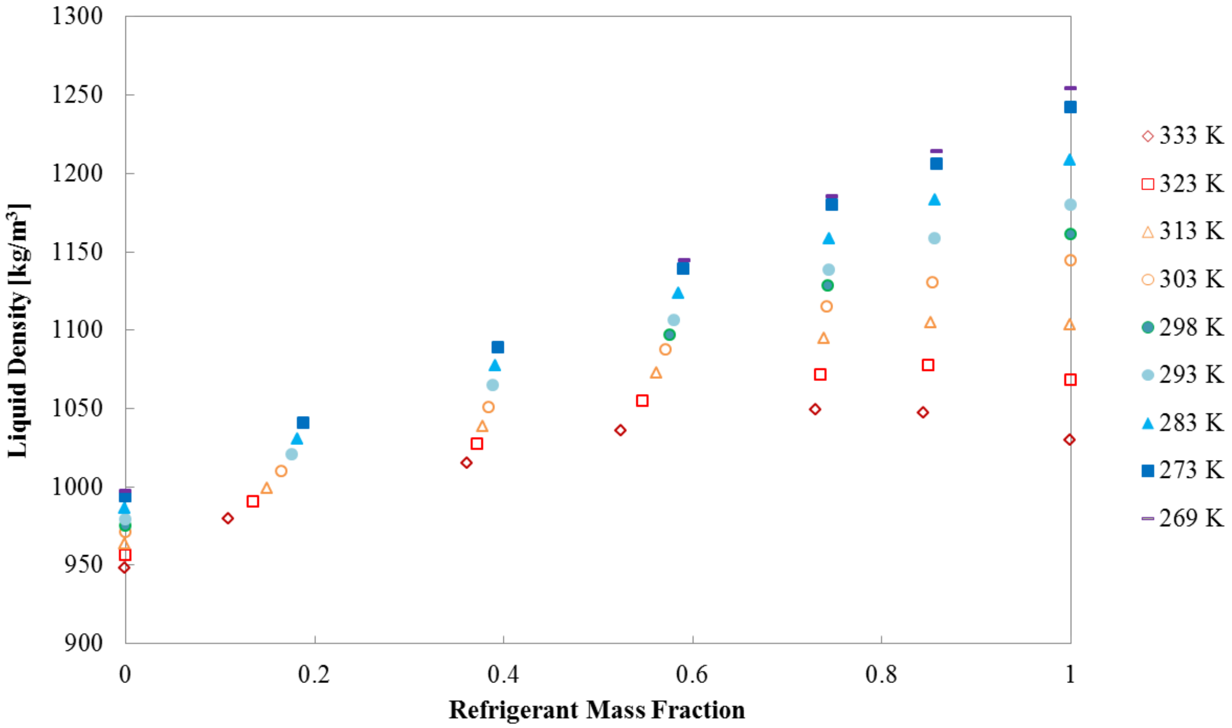


Figure 9: Saturated liquid density as a function of temperature for R-1234ze(E)/RL68H

R-1234ze(E) is attractive as a drop-in replacement for R-134a because it has similar thermophysical properties while being more environmentally friendly. Thermal conductivity, specific heat, viscosity, and latent heat values are similar for the pure refrigerants according the EES fluid property database. Thermal conductivity and viscosity values for R-1234ze(E) are estimated using and extended corresponding states approach. Additionally, similar P-T-ρ behavior suggests that R-1234ze(E), and R-1234yf, could be used in the same systems currently designed for R-134a with similar performance. Numerous experimental studies have been undertaken to evaluate the performance of HFOs like R-1234ze(E) as a drop-in replacement for R-134a [7-11]. Mixture properties of the refrigerant and a compatible lubricant will allow for analytical performance comparisons and ease the need for extensive experimentation.

The VLE data for R-1234ze(E)/RL68H obtained in this study have been plotted with the VLE data for R-134a/RL68H reported by Martz [38] in Figures 10 and 11 for comparison, where blue markers represent R-134a/RL68H and black markers represent R-1234ze(E)/RL68H mixtures.

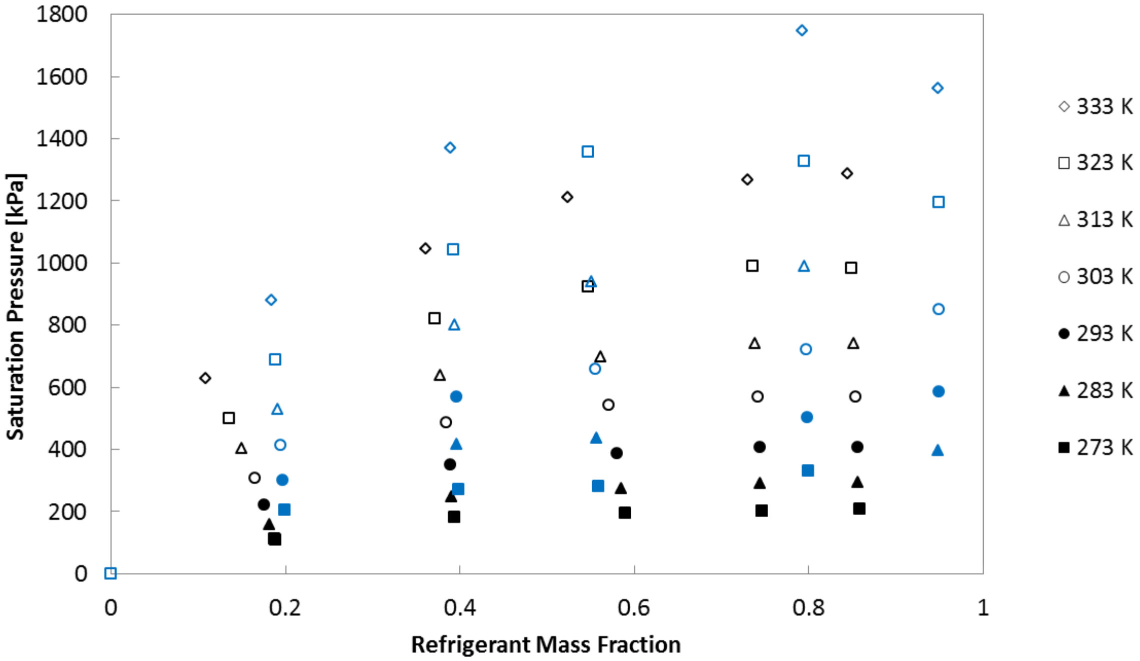


Figure 10: Saturation pressure data for R-134a (blue) and R-1234ze(E) (black) with RL68H

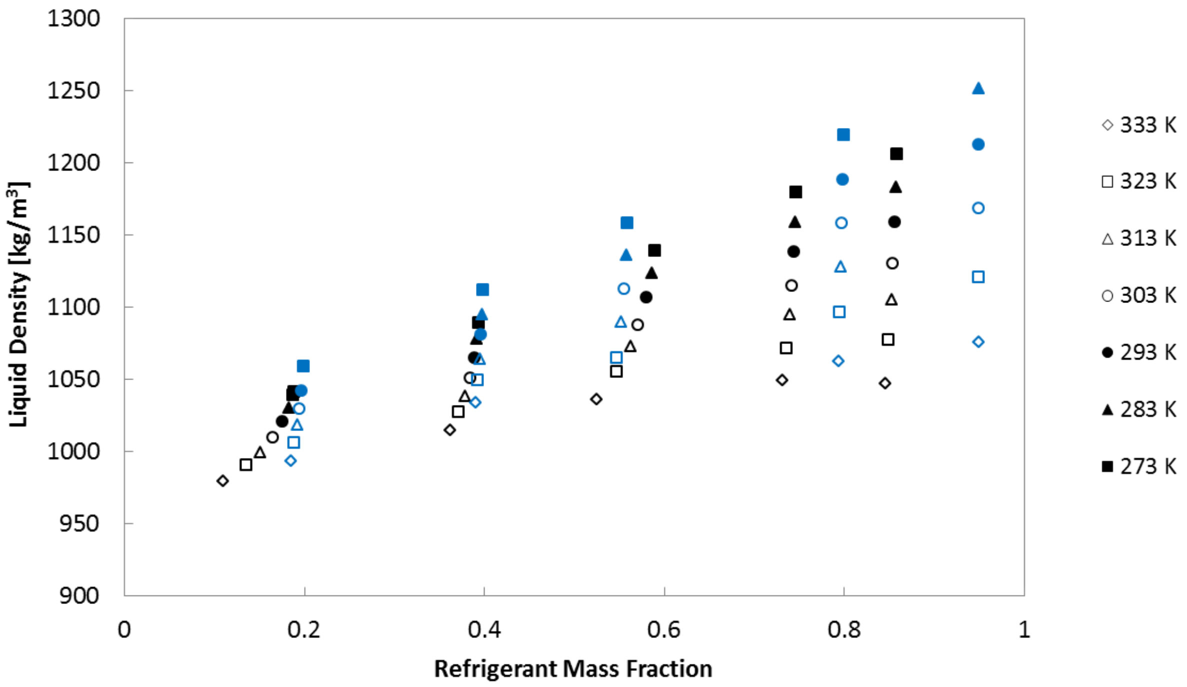


Figure 11: Saturated liquid density data for R-134a (blue) and R-1234ze(E) (black) with RL68H

The data show good agreement in the behavior of the two refrigerant/oil mixtures. The R-1234ze(E)/RL68H mixture has lower saturated liquid densities than does the mixture with R-134a, and only slightly lower saturation pressures. These results are expected from the slight difference in saturation pressures of the pure-refrigerant components. The good agreement of *P*-*T*-*ρ*-*x* data suggests that similar modeling methods may work for the new refrigerant despite the difference in molecular structure.

Chapter 4 – Mixture Analysis

Real fluids can exhibit non-ideal behavior. In a two-phase mixture, such as occurs at saturated conditions of a binary mixture, non-idealities may occur in the vapor phase, in the liquid phase, and in the mixing behavior. In order to account for these non-idealities, several “correction” terms must be included in the thermodynamic analysis of the mixture. Non-ideality in the vapor phase, or deviation from ideal gas behavior, is expressed using the vapor fugacity. In addition to the fugacity, the Poynting effect, a term that accounts for pressure-dependent changes in liquid fugacity, accounts for the liquid phase non-ideality. The mixture non-ideality is then expressed using the activity coefficient, in terms of the vapor- and liquid-phase non-idealities. Such an analysis is often referred to as an activity-fugacity (γ-ϕ), model.

4.1 Vapor Phase Non-Ideality

The widely used two-parameter cubic Peng-Robinson equation of state (PR-EOS) [65] has successfully described refrigerants and shown good results when used with activity coefficient models of refrigerant/oil mixtures [24, 32, 38-40, 52, 68]. The PR-EOS takes the convenient form

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v\left(v+b\right)+b\left(v-b\right)} \tag{7}$$

where

$$a = 0.45724\frac{\left(RT_c\right)^2}{P_c} \tag{8}$$

$$b = 0.07780\frac{RT_c}{P_c} \tag{9}$$

$$\alpha = \left(1 + \kappa\left(1 - \sqrt{\frac{T}{T_c}}\right)\right)^2 \tag{10}$$

and *κ* is a function of the acentric factor that can be determined experimentally or approximated using existing correlations, and parameters *a* and *b* are functions of the critical properties. Like most equations of state, the Peng-Robinson equation of state fails near the critical point. Reduced temperatures in this study remained below 0.90 to avoid performance problems near the critical point.

Using the PR-EOS, the fugacity coefficient for the refrigerant in the vapor phase can be described in terms of the compressibility factor, *Z*, by the following simplified equation

$$\ln(\Phi_r) = Z - 1 - \ln(Z - B) - \frac{A}{2B\sqrt{2}}\ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right) \tag{11}$$

where $$A = \frac{a\alpha P}{(RT)^2} \tag{12}$$

$$B = \frac{bP}{RT} \tag{13}$$

This simplified expression for fugacity coefficient assumes that only refrigerant is found in the vapor phase ($y_r=1$). The assumption is validated by the significant difference in saturation pressures of refrigerants and lubricants [69]. Thermodynamic background information regarding the fugacity coefficient can be found in Appendix B.

Results for the fugacity coefficient of R-1234ze(E) for the five mixture compositions included in this study are presented in Figure 12, as a function of temperature and bulk refrigerant mass fraction.

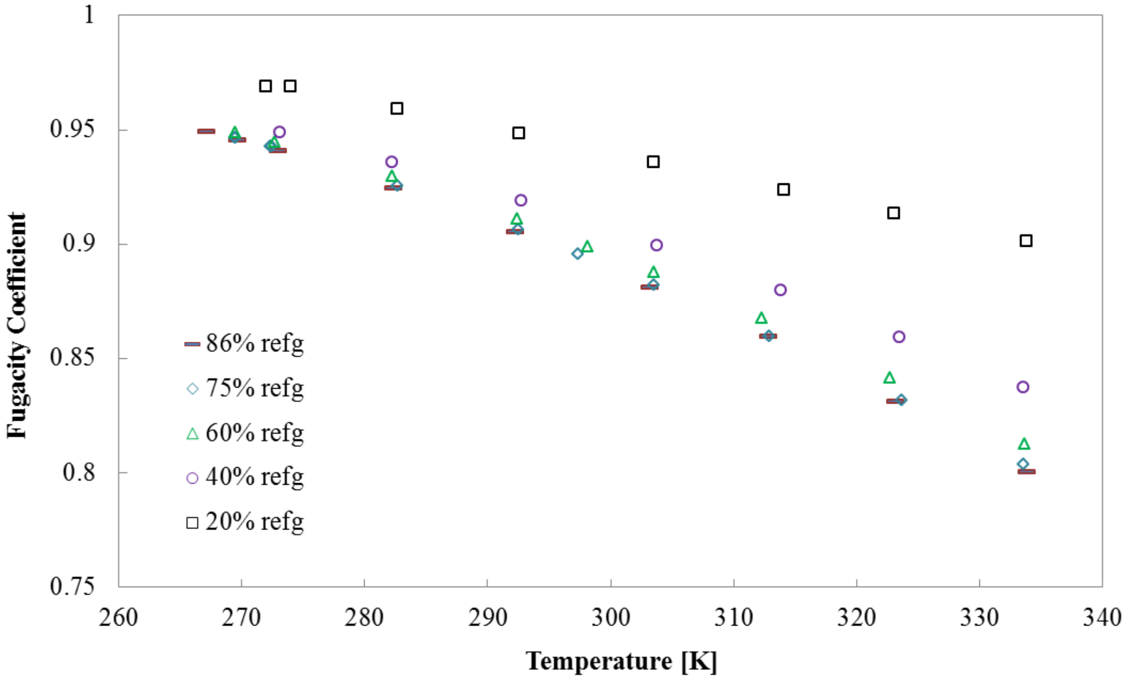


Figure 12: Fugacity coefficients as a function of temperature and bulk refrigerant mass fraction for R-1234ze(E)/RL68H

Non-idealities, as indicated by deviations from unity, increase with temperature and refrigerant concentration. As temperature and refrigerant concentration decrease, the corresponding vapor pressure is lower and the vapor exhibits behavior closer to that of an ideal gas.

4.2 Liquid Phase Non-Ideality

The liquid phase non-ideality can also be expressed in terms of fugacity but requires and additional correction factor. The Poynting effect, *Pe*, represents changes in the liquid fugacity due to vapor pressure, or non-idealities in the liquid phase.

$$Pe = \exp\left(\frac{v_{liq,sat}\left(P - P_{sat}\right)}{RT}\right) \tag{14}$$

where $v_{l,sat}$ is assumed to be the saturated liquid specific volume at mixture temperature. This assumption holds for most liquids, including refrigerants and oils, except near the critical point. *Pe* accounts for differences in system and saturation pressure, or the resulting superheating/subcooling of a component in a mixture.

Values for the Poynting effect for R-1234ze(E)/RL68H at various temperatures and concentrations are presented in Figure 13.

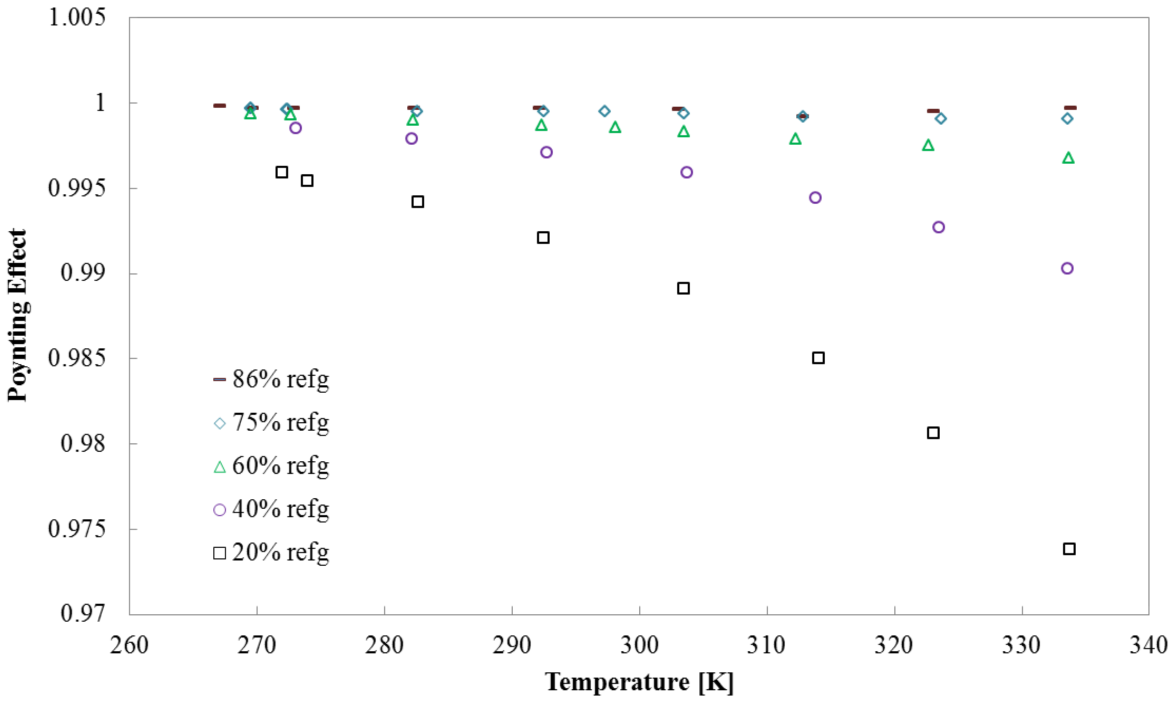


Figure 13: Poynting effect as a function of temperature for R-1234ze(E)/RL68H

The Poynting effect is most important for the mixtures with the highest oil concentrations. While there is some deviation from unity at higher temperatures, the value remains nearly equal to one for mixtures with higher refrigerant concentrations. Values below unity indicate superheating of the refrigerant due to the presence of the lubricant. For refrigerant/oil mixtures with high refrigerant concentrations, the Poynting effect may be negligible.

4.3 Mixture Non-Ideality

The activity coefficient, used to evaluate the non-ideal mixture behavior, can be calculated from experimental data using the following:

$$\gamma_r = \frac{y_r P \Phi_r}{x_r P_{sat} \Phi_{r,sat} Pe} \tag{15}$$

where γ_r is the activity coefficient of the refrigerant and the saturated properties are evaluated for the pure refrigerant component. In refrigerant/oil mixtures, the saturation pressures of the oil is significantly lower than the refrigerant, allowing the vapor phase to be assumed as pure refrigerant (y_r=1). Thermodynamic details regarding activity and the activity coefficient can be found in Appendix B.

According to Spauchus [69], the activity of a binary refrigerant/oil mixture is more sensitive to the mole fraction than temperature. The relative insensitivity to temperature can be seen in Figure14, where activity values for temperatures ranging from 0°C to 60°C are shown as a function of mole fraction of refrigerant in the liquid phase.

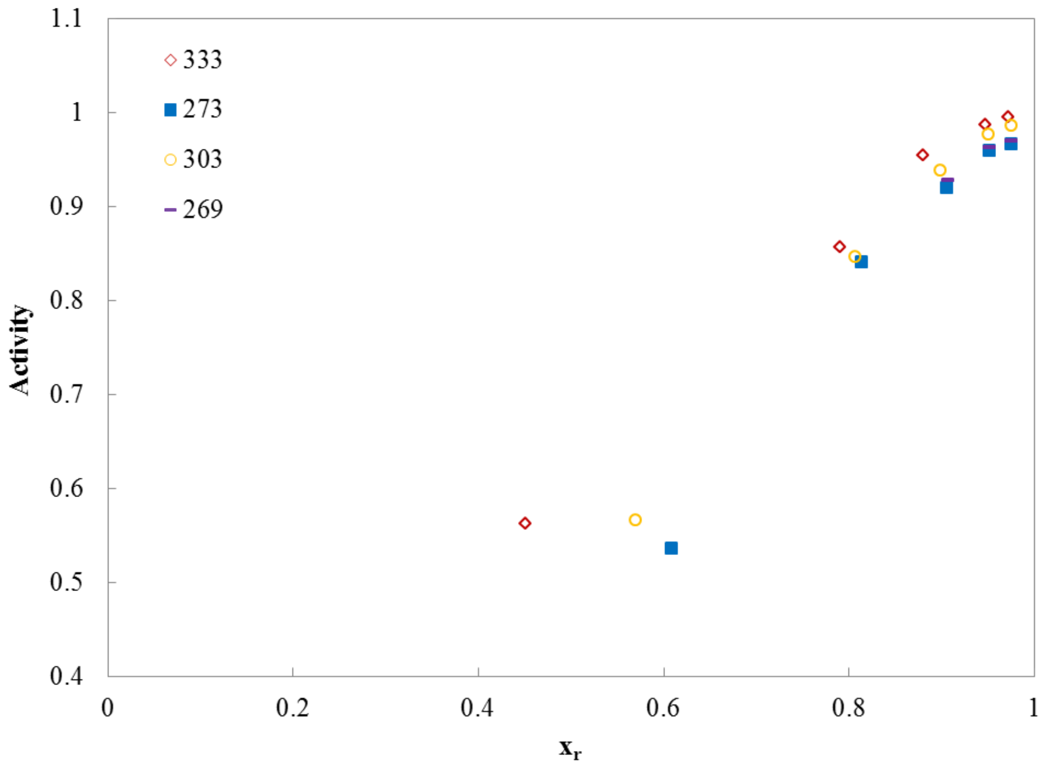


Figure 14: Activity values and refrigerant mole fractions for R-1234ze(E)/RL68H

Binary refrigerant/oil mixtures can be classified into one of three categories based on the activity coefficient. One category of mixtures has activity coefficients greater than one, or positive deviations from Raoult's law. The forces between like molecules are stronger than those between unlike molecules for these mixtures. A second category of mixtures has activity coefficients less than unity, and the forces between unlike molecules are dominant. Polymer solutions usually fall into this category. The third category exhibits both positive and negative deviation from Raoult's law. R-134a/POE mixtures have been classified as part of this third category [38, 41]. Similarly, data for the R-1234ze(E)/RL68H mixtures are described by the third category, as shown in Figure 15.

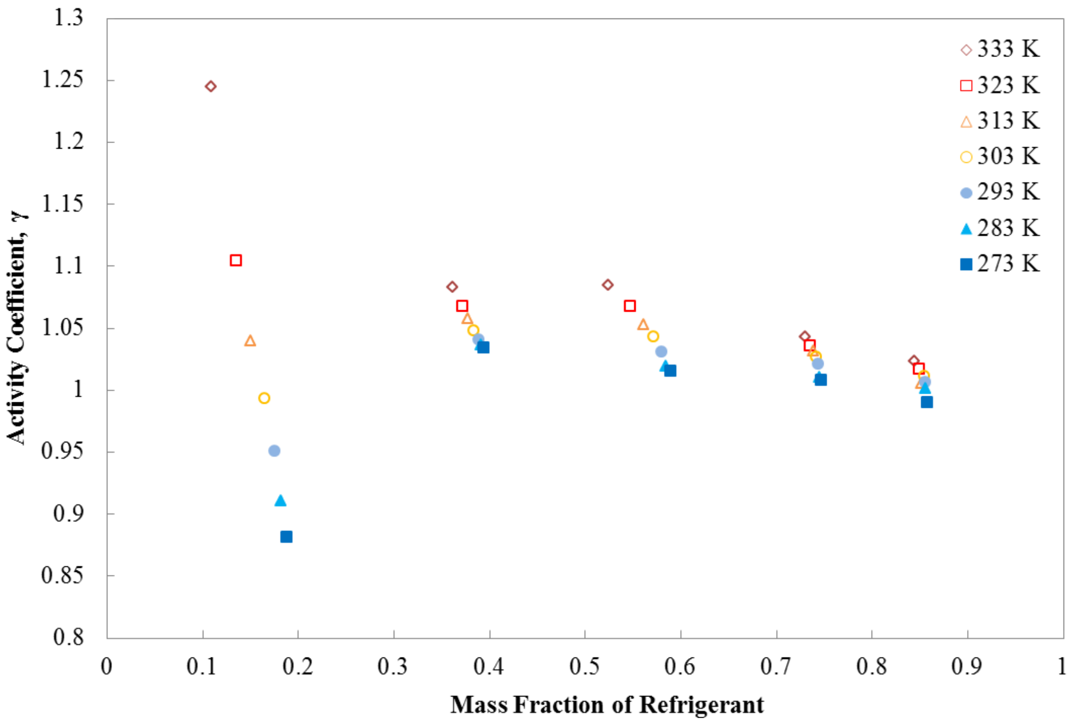


Figure 15: Activity coefficient as a function of refrigerant mass fraction

Experimental results for the activity coefficient can be correlated using mixture models, such as the ones described in Chapter 5.

4.4 Uncertainty

Calculated values for the activity and fugacity coefficient uncertainties resulting from the measurement uncertainties reported in Chapter 2. The propagation of uncertainty was calculated using Engineering Equation Solver (EES), assuming 2σ gives a 95% CI. The uncertainties for the calculated values based on experimental data are given in Table 2.

Results are presented for a typical case and for the worst case. Worst case corresponds to the lowest refrigerant concentration (20%) and highest temperature (60°C), except for the activity coefficient. The worst case for the activity coefficient occurs at the lowest temperature of the entire data set (-6°C), which corresponds to the lowest saturation pressure. The instrument used to measure pressure has an absolute error associated with it, rather than a relative error. The absolute error results in a highest percent error in pressure measurements for the lowest pressure. Accordingly, the uncertainty in activity was greatest at the lowest temperature for each mixture.

Table 2: Uncertainty in calculated values

Variable	**Typical Case**	**Worst Case** ***(conditions)***
Activity coefficient, γ	0.005 (0.5%)	0.014 (1.6%) *(60°C x=20)*
Poynting effect, *Pe*	7.5E-05 (.008%)	0.0001 (0.01%) *(60°C x=20)*
Refrigerant mass fraction (liquid phase)	0.0004 (.05%)	0.002 (1.8%) *(60°C x=20)*
Refrigerant mole fraction (liquid phase)	0.00007 (0.01%) <50% oil 0.00063 (0.07%) >50% oil	0.005 (1%) *(60°C x=20)*
Activity	0.004 (0.3%)	0.009 (0.98%) *(-6° C x=0.85)*

It is important to select accurate instruments for the experimental range covered when measuring thermophysical properties.

Chapter 5 – Mixture Theories & Model Comparison

5.1 Mixture Theories

Mixture modeling can be used to predict thermophysical properties of multicomponent mixtures at given conditions. Accurate mixture models eliminate the need for extensive experimentation in order to describe mixture behavior. Often, these models are semi-empirical and rely on an initial set of data to fit the model. The intermolecular interactions between the fluids, and the intramolecular interactions within the individual fluids both have an impact on mixture behavior. The contributions of these interactions may shift as dissimilarities in the component molecules become more pronounced.

Various models exist for vapor liquid equilibria predictions for mixtures, including EOS models, activity-coefficient models, strictly empirical models, molecular models, and EOS models combined with excess free energy (or liquid activity coefficient), EOS-G^{ex} models, and completely predictive models based on molecular structures and fields.

For refrigerant/lubricant mixtures, the properties of the pure refrigerant are generally well-characterized. In the event of a refrigerant phase-out, such as the current phasing-out of R-134a, new refrigerants may require further experimentation to determine accurate fluid descriptions. On the other hand, the refrigerant lubricant description is often lacking due to proprietary concerns and the low vapor pressures. Commercial lubricants typically contain additive packages for enhanced performance, but the additives are not disclosed by the manufacturers, further obfuscating the lubricant properties. Lacking sufficient property data on the lubricants, modeling methods such as the completely predictive methods and group contribution methods like UNIFAC may not be appropriate.

For binary mixtures including lubricants, modeling methods such as the activity coefficient models are useful because extensive knowledge of both components is not required. Activity coefficient (excess free-energy) models can depend on the bulk composition (i.e. Redlich-Kister, Margules, Wohl, and van Laar) of the solution or the local composition around molecules in the solution (i.e. Wilson, Heil, and NRTL). The local composition models generally describe non-ideal mixture properties better than those based on bulk composition without requiring additional parameters [52].

In this study, the Wilson, Heil, NRTL, and UNIQUAC relations are correlated with experimental data for the R-1234ze(E)/RL68H mixture. The performance of the models will then be evaluated and compared.

5.1.1 Wilson Model

The Wilson method for local composition modeling of mixtures is one of the most well known and widely used. Wilson derived an expression for the Gibbs energy for non-ideal solutions, which could be extended to multicomponent mixtures by modifying the number of interaction parameters. The model requires *n(n-1)* interaction parameters for a mixture with *n* components; thus for a binary mixture, two interaction parameters are required.

Wilson’s semi-empirical relation is based on the local compositions within a mixture, which are described by the following equations with terms similar to the Boltzmann distribution:

$$\frac{x_{12}}{x_{11}} = \frac{x_2}{x_1} \frac{\exp\left(-\frac{\lambda_{12}}{R_u T}\right)}{\exp\left(-\frac{\lambda_{11}}{R_u T}\right)} \tag{16}$$

$$\frac{x_{21}}{x_{22}} = \frac{x_1}{x_2} \frac{\exp\left(-\frac{\lambda_{21}}{R_u T}\right)}{\exp\left(-\frac{\lambda_{22}}{R_u T}\right)} \tag{17}$$

Where x_{ij} denotes the local composition, as a mole fraction, of component *i* around component *j.* The local compositions are related as follows:

$$x_{12} + x_{11} = 1 \tag{18}$$

$$x_{21} + x_{22} = 1 \tag{19}$$

The term λ_{ij} represents the interaction energy of molecule *i* on component *j*, and λ_{ij} is equal to λ_{ji}. By expressing the interaction energy parameters in terms of their differences, the model can be solved for a binary mixture knowing two parameters: λ_1 and λ_2.

$$\lambda_1 = \lambda_{21} - \lambda_{11} \tag{20}$$

$$\lambda_2 = \lambda_{12} - \lambda_{22} \tag{21}$$

The expression for the excess molar Gibbs energy in terms of the local mole fractions is shown in Eq. (22).

$$\frac{g^E}{R_u T} = -x_1 \ln\left(x_1 + x_2\Lambda_{12}\right) - x_2 \ln\left(x_2 + x_1\Lambda_{21}\right) \tag{22}$$

where

$$\Lambda_{12} = \frac{\overline{v}_2}{\overline{v}_1} \exp\left(-\frac{\lambda_2}{R_u T}\right) \tag{23}$$

$$\Lambda_{21} = \frac{\overline{v}_1}{\overline{v}_2} \exp\left(-\frac{\lambda_1}{R_u T}\right) \tag{24}$$

The activity coefficient can then be described by the following expression using the Wilson model [62],

$$\ln\left(\gamma_1\right) = -\ln\left(x_1 + x_2\Lambda_{12}\right) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}}\right) - \left(\frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \tag{25}$$

The adjustable parameters, Λ_{12} and Λ_{21}, are functions of the binary interaction parameters determined from the model fitting. If the binary interactions parameters are equal for a binary mixture, then the model reduces to the Flory-Huggins relation for polymer solutions. The adjustable parameter Λ_{ij} has physical meaning that describes mixture behavior. A positive value for Λ_{ij} corresponds to a positive deviation from Raoult's law, and a negative value indicates a negative deviation. A negative deviation from Raoult's law indicates that the adhesive forces between unlike components are stronger than the average cohesive forces between like components.

The Wilson model does not account for liquid-liquid equilibrium, rendering it inapplicable for mixtures exhibiting immiscible and partially miscible behavior. However, it has been shown that Wilson's model can describe partially miscible systems by dividing the interaction energies by a constant [63, 70]. Renon and Prausnitz (1968) [63] proposed using half the coordination number of the liquid and incorporated this modification when developing the NTRL model.

5.1.2 NRTL Model

The non-random two-liquid (NRTL) model was developed as a modification of Wilson's equation by introducing a third parameter that accounts for "non-randomness of the liquid solutions" [63]. The three-parameter relation for the activity coefficient using NRTL is

$$\ln\left(\gamma_1\right) = x_2^2\left(\tau_{21}\left(\frac{\Lambda_{21}}{x_1 + x_2\Lambda_{21}}\right)^2 + \frac{\tau_{12}\Lambda_{12}}{\left(x_1\Lambda_{12} + x_2\right)^2}\right) \tag{26}$$

$$\Lambda_{12} = \exp\left(-\alpha_{12}\tau_{12}\right) \tag{27}$$

$$\Lambda_{21} = \exp\left(-\alpha_{21}\tau_{21}\right) \tag{28}$$

The adjustable parameters, Λ_{12} and Λ_{21}, are functions of τ_{12} and τ_{21}.

$$\tau_{12} = \frac{\lambda_{12} - \lambda_{21}}{R_u T} \quad (29)$$

$$\tau_{21} = \frac{\lambda_{21} - \lambda_{12}}{R_u T} \quad (30)$$

The binary interaction parameters determined from the model fitting are used to calculate τ_{12} and τ_{21}; α_{12} and α_{21} are equal and represented as an empirical constant. When α_{12} and α_{21} are equal to zero, the activity coefficient equation reduces to the two-suffix Margules equation, and the solution is considered to be completely random. A value of 0.5 provided the best results for refrigerant/oil mixtures [38], so this value was adopted in the current study. A value of negative one for α_{ij} results in a special case known as the local effective mole fraction (LEMF) model [71]. The LEMF model can only describe mixtures with excess entropies greater than zero, which is not true for all refrigerant/oil solutions [69, 72].

5.1.3 UNIQUAC Model

The Universal Quasi –Chemical (UNIQUAC) theory incorporates local composition and structural parameters of the mixture components [64]. The UNIQUAC relation was developed as an extension to Guggenheim's quasi-chemical theory, providing applicability for molecules of different sizes. The UNIQUAC model can represent mixtures with molecules of different sizes and full- to partial-miscibility while still only requiring two parameters per binary system.

The UNIQUAC equation for activity coefficient is comprised of a combinatorial part and a residual part.

$$\ln\left(\gamma_r\right) = \gamma_r^c + \gamma_r^r \tag{31}$$

The combinatorial component is based on the molecular structure and sizes of the mixture components and concentration. All parameters in the combinatorial component are determined by molecular composition, mixture composition, and molecular structure of the mixture components.

$$\gamma_r^c = x_r \ln\left(\frac{\varphi_r}{x_r}\right) + x_o \ln\left(\frac{\varphi_o}{x_r}\right) + \frac{n_c}{2}\left(q_r x_r \ln\frac{\theta_1}{\varphi_r} + q_o x_o \ln\frac{\theta_2}{\varphi_o}\right) \tag{32}$$

The residual component accounts for the interaction of the molecules in the mixture and has a form similar to the variable parameters in the Wilson and NRTL models.

$$\gamma_r^r = -q_r x_r \ln\left(\theta_1 + \theta_2\tau_{21}\right) - q_o x_o \ln\left(\theta_2 + \theta_1\tau_{12}\right) \tag{33}$$

In addition to the variable parameters τ_{12} and τ_{21}, the UNIQUAC model contains the following variables based on fixed parameters

$$\varphi_r = \frac{r_1 x_r}{r_1 x_r + r_2 x_o} \tag{34}$$

$$\varphi_o = \frac{r_2 x_o}{r_1 x_r + r_2 x_o} \tag{35}$$

$$\theta_1 = \frac{q_r x_r}{q_r x_r + q_o x_o} \tag{36}$$

$$\theta_2 = \frac{q_o x_o}{q_r x_r + q_o x_o} \tag{37}$$

where r_i and q_i are fixed structural and size parameters for species *i*, respectively, and n_c is the coordination number, which is taken to be 10 [33, 42]. The values for the structural and size parameters are based on the chemical groups that comprise a species. Each species is described by its chemical groups with known bond angles and lengths. The parameter values for each species are summations of the values for the individual chemical groups of the molecule. More details about the UNIQUAC parameters can be found in Appendix C.

The UNIQUAC theory relies on information about the molecular structure for each component. The long-chain molecules, non-uniform character, and lack of detailed molecular information for refrigerant lubricants can limit the accuracy of UNIQUAC predictions for refrigerant/oil mixtures. However, the UNIQUAC theory has been shown to adequately predict VLE data and miscibility gaps of refrigerant/oil mixtures, even with the limited information available for lubricants [61, 73].

With new refrigerant molecules, chemical group information may be incomplete, requiring the estimation of some UNIQUAC parameters. This could also limit the applicability of UNIQUAC theory for alternative refrigerant/oil mixtures.

5.1.4 Heil Model

The activity coefficient expression proposed by Heil & Prausnitz [45] combines terms from both the Wilson and NRTL models. The model was developed to represent solutions of polymers in mixed solvents and solutions with polar and hydrogen-bonded components. The Flory-Huggins equation had proven inadequate for describing these solutions and other theories that had been presented as alternatives were more sophisticated and required multiple parameters.

The semi-empirical Heil equation requires only two parameters for multicomponent mixtures, as defined by Eqs. (39-40). The activity coefficient is determined by Eq. (38), where the first two terms of the expression come from Wilson’s local composition model, and the final term is equal to the NRTL relation.

$$\begin{aligned} \ln\left(\gamma_r\right) &= -\ln\left(x_1 + x_2\Lambda_{12}\right) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) + \ldots \\ &\ldots + x_2^2\left(\tau_{21}\left(\frac{\Lambda_{21}}{x_1 + x_2\Lambda_{21}}\right)^2 + \frac{\tau_{12}\Lambda_{12}}{\left(x_1\Lambda_{12} + x_2\right)^2}\right) \end{aligned} \tag{38}$$

where

$$\tau_{12} = \frac{\lambda_{12} - \lambda_{21}}{R_u T} \tag{39}$$

$$\tau_{21} = \frac{\lambda_{21} - \lambda_{12}}{R_u T} \tag{40}$$

The Heil model has proven more accurate than other mixture models for various refrigerant/oil mixtures [38, 39].

5.1.5 Other Models

An ideal solution can be described by Raoult's law, where the mixture pressure is dependent on the vapor pressure and mole fraction of a single, pure component. Such a relation would be convenient for refrigerant/oil mixtures where saturation pressures of pure refrigerants are generally well-characterized.

$$P = P_{1,sat} x_1 \tag{41}$$

Most real mixtures do not exhibit ideal solution behavior, leading to more complicated modeling methods using the activity coefficient, such as the local composition models described above. However, a recent study shows good agreement for predicted mixture pressures using Raoult's law for another HFO-refrigerant/POE lubricant binary mixture [46]. If Raoult's law provides accurate predictions for multiple components of HFO/POE mixtures, it would eliminate the need for more complicated modeling techniques for this new family of refrigerants. Because Raoult's law contains no adjustable interaction parameters, successful performance could lead to accurate mixture predictions with the need for limited validation with experiment data.

Equation of state correlations, such as the Peng-Robinson EOS combined with the one-parameter van der Waals (PR-1PVDW) mixing rule can also be used to describe mixture behavior. In the recent study of a different HFO/POE binary mixture, the PR-1PVDW model described the mixture pressure well, with a slight improvement over Raoult's law [46]. Equation of state models generally require detailed information about both components of a binary mixture, as well as experimental data to determine a binary interaction parameter.

Empirical correlations such as Redlich-Kister, van Laar, and Margules relations are generally not well-suited for refrigerant/oil mixtures due to their simplicity and need for similarity in molecule size and behavior. The widely-used Flory-Huggins polymer theory is a special case of the Wilson method, but was developed for polymer solutions where the size of one component may be several orders of magnitude larger than the other component. The size difference in most refrigerant and oil molecules is significantly smaller. If the Flory-Huggins theory were able to describe a mixture behavior better than the Wilson method, one could expect the Wilson interaction parameters to be equal, thus simplifying to the Flory-Huggins case.

Other local composition models have been proposed, including several modifications to the Wilson relation [74, 75]. In earlier vapor-liquid equilibrium studies of refrigerant/oil mixtures, the Wilson, Heil, or NRTL method outperformed other modified Wilson relations. If the selected models are unable to satisfactorily predict a binary mixture behavior, alternative models found in the literature can be evaluated.

The UNIFAC group contribution method requires more detailed knowledge of the lubricant, as do other purely predictive methods that aren't correlated with experiment data. Molecular modeling methods such as PC-SAFT, which has been used to successfully predict the VLE behavior of refrigerant blends, also require extensive knowledge of the molecular structures of all mixture components. The predictive models require more than two parameters and are more computationally expensive than local composition models and empirical correlations; they are not included in this study.

5.2 Model Fitting

Binary interaction parameters are required for comparing mixture model performance and must be determined for each mixture relation. First, values for activity coefficients are calculated using experiment data. For binary refrigerant/oil mixtures, the activity coefficient of the oil is unknown, requiring fitting of the mixture model to determine the two interaction parameters.

An objective function of the form

$$OBJ = \sum_{i=1}^{n} \left(\frac{\Theta_{cal,i} - \Theta_{\exp,i}}{\Theta_{\exp,i}} \right)^2 \tag{42}$$

where *n* is the number of experimental points and Θ can be pressure, activity coefficient, or concentration, has proven reliable; other objective functions which include measurement uncertainties can be tested for accuracy [37-40]. The objective function with θ as pressure was shown by Silverman and Tassios [76] to be the best of 10 objective functions for describing vapor liquid equilibria of 247 different binary systems, including earlier generations of refrigerant but not HFOs.

The binary interaction parameters were fit using the genetic algorithm available in Engineering Equation Solver (EES) [77]. Of the five optimization algorithms available with the software, the genetic method is the slowest but most robust. Unlike the other methods, the genetic method does not rely on carefully selected guess values, and it is designed to reliably locate a global optimum even when local optima are present. In order to ensure that the fit parameters corresponded to the global optimum, multiple optimizations were undertaken using various optimization methods, guess values, and parameter solution ranges. Once satisfied that the solution was near the global optimum, the binary interaction parameter solution range was reduced for a more focused search around the target optimum. The genetic optimization was then carried out for the maximum allowable number of generations and individuals in a population in the EES genetic algorithm (*i.e*. the most robust optimization in software package).

The shape of the objective function has been described in [38] and varies slightly based on the activity coefficient values. The mixture R-1234ze(E)/RL68H exhibited activity coefficients both greater than and less than one over the temperature and concentration ranges tested. For cases having mixed deviations from Raoult's law, as demonstrated by activity coefficient deviation from unity, the optimum root will continue to decrease very slightly as λ_1 gets larger.

A solution range for the binary interactions parameters of -20,000 to 20,000 was chosen; increasing the range by several orders of magnitude resulted in improvements within the uncertainty of the data.

5.3 Model Comparison

The experimental data for R-1234ze(E)/RL68H presented in Chapter 3 were used to determine binary interaction parameters for the four local composition vapor liquid equilibria models described earlier in Chapter 5. The resulting binary interaction parameters and model prediction error are described below.

5.3.1 Local Composition Model Predictions

The objective function selected to correlate the mixture models with experimental data can take many forms. An objective function based on the difference between experimental and predicted pressures, as shown in Eq. (43), has also been used to successfully correlate mixture models for refrigerant/oil mixtures and was adopted for this study.

$$OBJ = \sum_{i=1}^{n} \left(\frac{P_{cal,i} - P_{\exp,i}}{P_{\exp,i}} \right)^2 \tag{43}$$

This definition of the objective function was suggested by Silverman and Tassios [76] and used in many refrigerant/oil studies [37-39, 47-49]. The models were exercised with other objective functions, such as Eq. (43) with activity coefficient substituted for pressure. Minimizing Eq. (43) resulted in the best model performance.

The corresponding binary interaction parameters for each of the models are given in Table 3. The associated statistical quantities describing model performance, defined as percentages by Eqs. (44-46), are listed for each mixture model in Table 4.

$$\%AAD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{P_{cal,i} - P_{\exp,i}}{P_{\exp,i}}\right| \tag{44}$$

$$\%RMS = \frac{100}{N}\sqrt{\sum_{i=1}^{N}\frac{\left(P_{cal,i} - P_{\exp,i}\right)^2}{\left(P_{\exp,i}\right)^2}} \tag{45}$$

$$\%BIAS = \frac{100}{N}\sum_{i=1}^{N}\frac{P_{cal,i} - P_{\exp,i}}{P_{\exp,i}} \tag{46}$$

Table 3: Binary interaction parameters for R-1234ze(E)/RL68H correlated with pressure

Method	**λ_1**	**λ_2**
Wilson	20000.00	1908.00
Heil	-5966.60	7737.50
NRTL	-3082.72	7567.46
UNIQUAC	1662.81	1981.24

Table 4: Statistical parameters for R-1234ze(E)/RL68H correlated with pressure

Method	**%AAD**	**%RMS**	**%BIAS**	**Max % Deviation**
Wilson	3.885	1.010	0.722	28.8
Heil	1.967	0.445	-0.511	13.7
NRTL	2.983	0.798	-0.299	24.7
UNIQUAC	9.528	1.751	-1.427	28.0
Raoult's Law	3.551	0.884	-0.346	22.7

As seen in Figure 16, the relative deviations of the vapor pressure are within about 10% for refrigerant mass fractions higher than 0.25 for all models except UNIQUAC. The Heil model has the lowest RMS value, 0.45%, followed by NRTL and Raoult's law and with 0.80% and 0.88%, respectively. The Heil model clearly outperforms the other models listed in Table 4 for R-1234ze(E)/RL68H. However, Raoult's law shows agreement within 1% and is much simpler to implement with no adjustable parameters. For the greatest accuracy in pressure predictions, the Heil model should be used, but Raoult's law is recommended when an RMS value within 1% is acceptable.

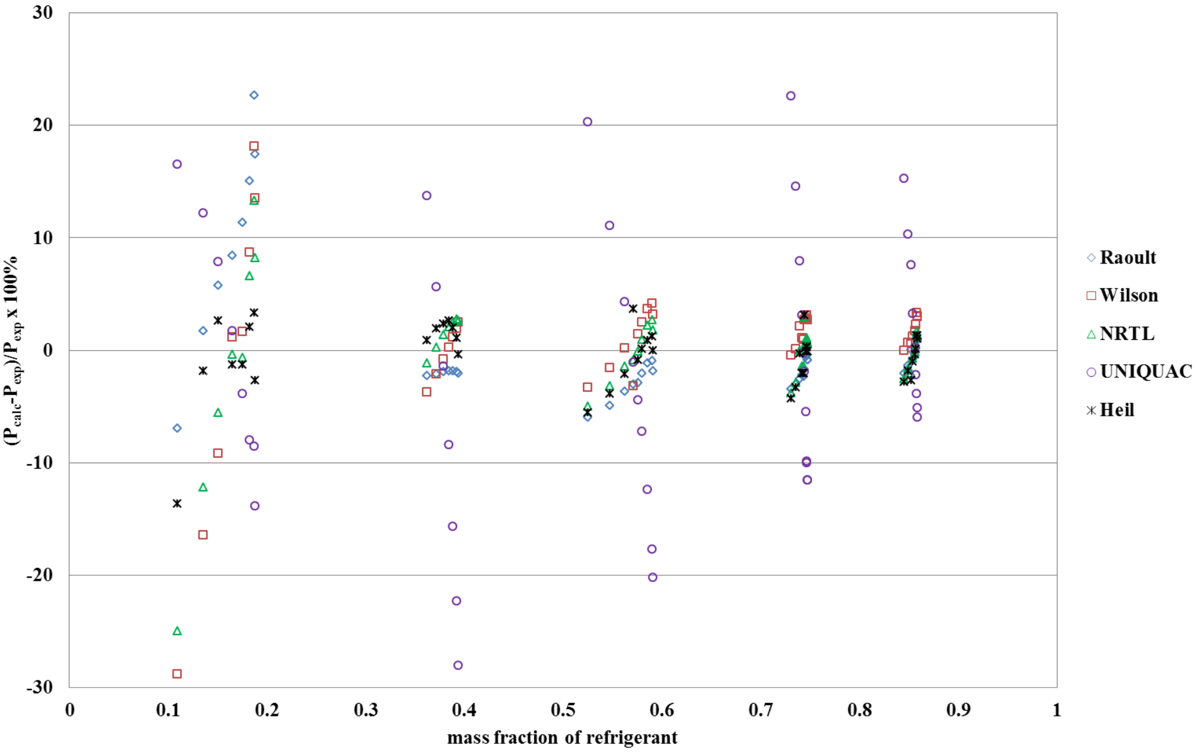


Figure 16: Relative deviations of vapor pressure predictions for R-1234ze(E)/RL68H

All models perform better at higher refrigerant concentrations and more poorly at high oil concentrations. As shown in Chapter 4, the activity coefficient deviation from unity was the greatest for lowest refrigerant concentrations; larger deviations in activity coefficient translate to more non-ideal behavior in the mixture solution. Additionally, data at the highest oil concentrations corresponded with the highest uncertainties for pressure and mole fraction of refrigerant in the liquid phase—thus to the highest uncertainty in activity coefficient. More accurate data for the mixture with the highest oil concentration might improve the accuracy of the mixture models, but non-idealities in the liquid phase would remain present at high oil concentrations. The Heil model predicts the non-ideal behavior of the mixture better than the four other models considered.

The models were compared again omitting data for the mixture with the highest oil fraction. Bulk mass refrigerant mass fractions of the included data were greater than 0.25. The revised results are given in Tables 5 and 6.

Table 5: Interaction parameters for R-1234ze(E)/RL68H (>25% refg.) correlated with pressure

Method	**λ_1**	**λ_2**
Wilson	4353.30	2185.57
Heil	-6301.25	8509.35
NRTL	-3617.55	8965.20
UNIQUAC	1324.39	2389.63

Table 6: Statistical parameters for R-1234ze(E)/RL68H (>25% refg.) correlated with pressure

Method	**%AAD**	**%RMS**	**%BIAS**
Wilson	1.171	0.344	0.286
Heil	1.406	0.296	-0.344
NRTL	1.353	0.279	0.087
UNIQUAC	9.606	1.950	-2.239
Raoult's Law	1.856	0.375	-1.676

As seen from the statistical parameters, the Wilson, NRTL, and Raoult's law perform nearly three times better when the experimental uncertainties are lower and refrigerant mass fractions are higher. The performance of the Heil and UNIQUAC models was not notably affected by using the reduced data set.

Relative deviations in vapor pressure predictions for R-1234ze(E)/RL68H mixtures with bulk refrigerant concentrations greater than 25% are presented in Figure 17. The less accurate UNIQUAC model results are omitted from the plot. Deviations are within about 4% for each model, with a maximum deviation of 6% occurring for Raoult's law.

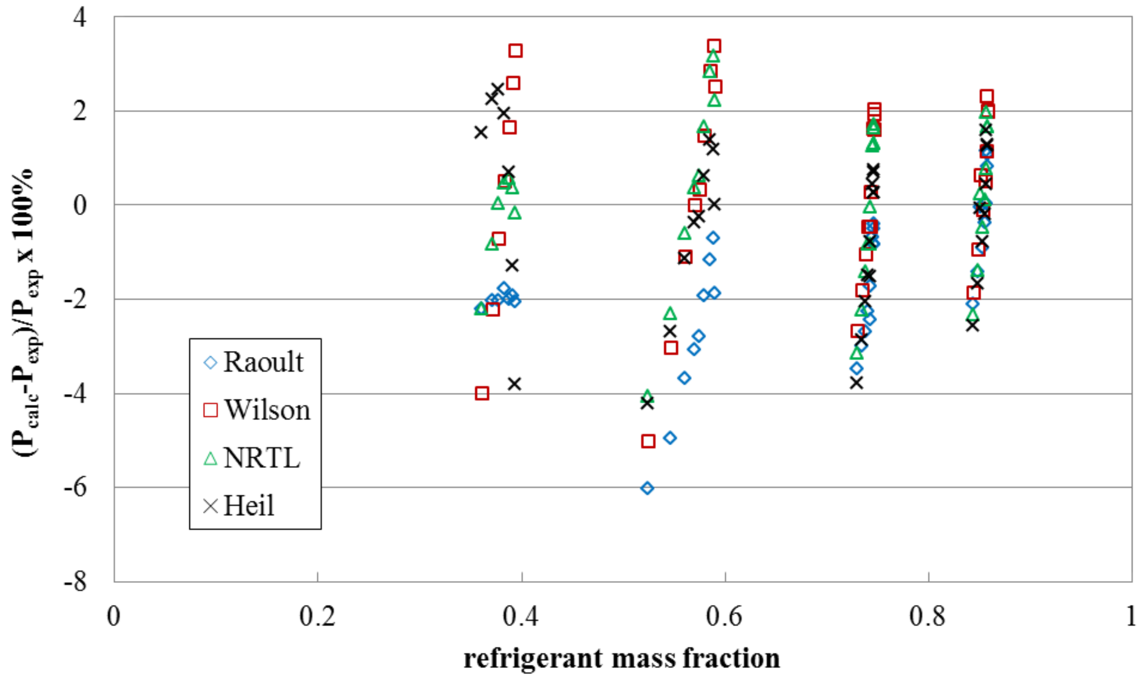


Figure 17: Revised relative deviations of vapor pressure predictions for R-1234ze(E)/RL68H

From the results described above, the NRTL model provides the most accurate description of R-1234ze(E)/RL68H mixtures, among the local composition models included in the study. However, Raoult's law predicts mixture pressure only slightly worse, and requires only knowledge of the mole fraction of refrigerant and the saturation pressure of the pure refrigerant at the system temperature. All models, except UNIQUAC, exhibit excellent agreement with the data subset, having comparable RMS values, within about 0.1%.

Generally, the interaction parameters were not significantly altered when using the subset of data, as shown in Table 7. However, one of the Wilson model parameters changed by an order of magnitude, indicating increased sensitivity to the data used for fitting model parameters. Wilson, NRTL, and Raoult performance exhibited a two- to three-fold improvement when using the subset of data, revealing sensitivity to mixture ideality. UNIQUAC and Heil performed similarly with and without the excluding data, indicating more consistent performance for non-ideal mixtures.

Table 7: Interaction parameters for R-1234ze(E)/RL68H with and without highest oil concentration

Method	**All Concentrations**		**Omitting x<25%**	
	λ_1	λ_2	λ_1	λ_2
Wilson	20000.00	1908.00	4353.30	2185.57
Heil	-5966.60	7737.50	-6301.25	8509.35
NRTL	-3082.72	7567.46	-3617.55	8965.20
UNIQUAC	1662.81	1981.24	1324.39	2389.63

In order to investigate model sensitivity with regard to binary interaction parameters, two comparisons were undertaken: one predicting R-1234ze(E)/RL68H behavior using model parameters fit for similar mixtures, and one based on a parametric study of model parameters.

The first method adopted newly fit model parameters for R-134a/RL68H to predict pressure for R-1234ze(E)/RL68H. New parameters were calculated using tabulated *P-T-x* data reported by Martz [38]. The original model parameters presented in Ref. [38] are provided in Table 8; new parameter values are listed in Table 9.

Table 8: Model parameters and performance reported by Martz

R-134a/RL68H	**λ_1**	**λ_2**	**2-sigma % error**
Wilson	18449	2510	9.5
Heil	4417	1122	7.1
NRTL	9498	-2784	12.6
UNIQUAC	79.8	1715	9.1

Table 9: New model parameters calculated with data from (Cite Martz)

NEW R-134a/RL68H	**λ_1**	**λ_2**	**%AAD**	**%RMS**	**%BIAS**
Wilson	20000	2536.34	3.923	0.754	-2.471
Heil	-3638.69	3918.62	7.682	1.292	-6.132
NRTL	-2823.05	10351.81	3.803	0.853	-2.219

Earlier highly-cited works in refrigerant/lubricant research [38, 39] provided only a 2-σ error to quantify model performance. Using tabulated data for measured and predicted pressures, the reported 2-σ errors did not correspond to any of the calculated statistical parameters. It is unclear how these values were determined from the provided data.

Using the P-T-x data and model parameters provided in [38], the mixture models were fit to evaluate %AAD, %RMS, and %BIAS for a more comprehensive comparison. The agreement with the models was significantly better than indicated by the reported values for 2-σ error; RMS error remained below 2% for Wilson, Heil, and NRTL models. Using the new model parameters, the Wilson model exhibits the best agreement with R-134a/RL68H data. It is unclear how the reported 2-σ errors reported by Martz and Jacobi were calculated, as they do not correspond to twice the RMS error. RMS values approach the reported 2-σ errors when the models are solved using refrigerant mass fraction in place of the refrigerant mole fraction; however, the reported error is still not replicated. The univariate optimization method applied in both studies may have provided parameter values corresponding to local minima rather than global minima, despite precautions taken by varying the initial guess values. This weakness would result in inflated error in model performance. Due to inconsistency in error-reporting and improved optimization methods, the new model parameters for R-134a/RL68H mixtures listed in Table 9 will be adopted hereafter.

As a potential replacement for R-134a, it is useful to see if existing models for mixtures including R-134a can be used to predict the behavior of mixtures including R-1234ze(E). One method for testing the applicability of current models is to use existing model parameters with the new mixtures including R-1234ze(E). The results for pressure predictions of R-1234ze(E)/RL68H mixtures using parameters optimized for R-134a/RL68H mixtures are presented in Table 10.

Table 10: Statistical parameters for R-1234ze(E)/RL68H predicted pressures using binary interaction parameter for models fitted with R-134a/RL68H data.

	Wilson	**Heil**	**NRTL**
λ_1	*20000.00*	*-3638.69*	*-2823.05*
λ_2	*2536.34*	*3918.62*	*10351.91*
%AAD	5.832	5.478	5.143
%RMS *(R134a)*	1.415 *(0.754)*	1.401 *(1.292)*	1.029 *(0.853)*
%BIAS	4.931	0.975	3.531

Comparing the results provided in Tables 4 and 10, the Wilson and NRTL models perform comparably with significantly different binary interaction parameters. The Heil model performs significantly worse when the binary interactions parameters deviate from the fitted values. However, all models have an RMS error less than 1.5%, indicating very good fits.

The Wilson model parameters were similar for both sets of mixtures; Heil model parameters maintained the same order of magnitude; but one NRTL parameter changed by an order of magnitude. Satisfactory model performance with varying sets of model parameters may indicate a lack of sensitivity to parameter selection. A range of parameter values may produce acceptable results, requiring less costly fitting. When using genetic algorithms, fewer generations and individuals would significantly reduce computation time while maintaining satisfactory performance. Optimization parameters could be selected based on the accuracy desired.

The second method of examining model sensitivity utilized the VLE data for R-1234ze(E)/RL68H. Akin to the univariate approach, a test matrix of model parameters was used to calculate mixture pressure. The test matrix and results for the Wilson model is given in Table 11. Similar tables for the NRTL and Heil models can be found in Appendix E.

Table 11: Evaluation of Wilson model sensitivity to adjustable parameters

λ_1	**λ_2**	**%AAD**	**%RMS**	**%BIAS**	**%max dev**
-10000	-10000	92.927	14.041	-92.927	100
	-100	27.199	5.583	-27.199	85
	0	26.581	5.490	-26.581	85
	100	25.973	5.397	-25.973	85
	10000	5.625	1.330	-5.154	38
-100	-10000	92.683	14.003	-92.683	99
	-100	20.151	4.032	-20.151	65
	0	19.356	3.894	-19.356	64
	100	18.568	3.756	-18.568	63
	10000	15.120	4.533	14.043	68
0	-10000	92.678	14.002	-92.678	99
	-100	20.053	4.014	-20.053	65
	0	19.255	3.876	-19.255	64
	100	18.466	3.738	-18.466	63
	10000	15.308	4.583	14.268	81
100	-10000	92.674	14.001	-92.674	99
	-100	19.956	3.997	-19.956	65
	0	19.156	3.859	-19.156	64
	100	18.364	3.720	-18.364	63
	10000	15.492	14.490	4.632	82
10000	-10000	92.414	13.963	-92.414	99
	-100	15.689	3.396	-15.469	60
	0	14.852	3.247	-14.596	59
	100	14.023	3.098	-13.730	58
	10000	23.138	6.169	23.138	101
20000 (this work)	**1908 (this work)**	**3.885**	**1.010**	**0.722**	**29**

The results shown in Table 11 suggest that the Wilson model is fairly insensitive to parameter values except at the imposed limits (-10,000 and 10,000) of λ_2, where performance degrades. The outlying low RMS value for λ_1=-10,000 and λ_2=10,000 indicated the presence of another root, or local minima in the model. Generally, the Wilson model can predict pressures for R-1234ze(E)/RL68H mixtures within 5% RMS (10% error, 95% CI), which is three- to four-times worse than the optimized performance of 1.01% RMS. Depending on the accuracy desired for a particular application, optimized parameters may not be required.

A similar table for the Heil model reveals analogous behavior. The RMS values for the Heil model are less than 2% except when λ_1=-10,000. Like the Wilson model, optimized RMS values for the Heil model are about three- to four-times better than the general results for parameters within the -10,000 to 10,000 range.

Like the Wilson and Heil models, NRTL performance is worst when λ_1=-10,000. A slight degradation in performance also occurs when λ_2=10,000 or -10,000. Otherwise, RMS values for the NRTL model are nearly uniform at approximately 1%. The general case is only slightly better than the optimized RMS, 0.798%.

Based on the results presented in the three tables, model performance is surprisingly insensitive to parameter value selection for a parameter space ranging from -10,000 to 10,000. The NRTL model is the least sensitive to parameter values. Agreement comparable to the optimized results for R-1234ze(E)/RL68H mixtures can be obtained by randomly selecting values for λ_1 and λ_2, where λ_1>-10,000 and -10,000< λ_2<10,000. The RMS value for general cases with NRTL is the lowest of the three models considered. The fact that NRTL performance is near-optimum for a wide range of parameter values supports the selection of NRTL when choosing a mixture model.

5.3.2 Ideal Solution Approximations

The remarkable agreement with Raoult's law suggests that R-1234ze(E)/RL68H mixtures behave like an ideal solution. With this in mind, expressions for ideal solution density may also successfully predict R-1234ze(E)/RL68H liquid density values. Equations for ideal solutions can be quickly evaluated at little computational expense. Unlike Raoult's law, density expressions for ideal solutions require some knowledge of both components of a binary mixture. A temperature dependent curve-fit for RL68H density data provided by Martz [33] is adopted in the following analysis.

Two methods for calculating the density of an ideal solution were evaluated using the R-1234ze(E)/RL68H mixture data provided in Chapter 3. The first method is based on the assumption that the volume of the solution is proportional to the mass and that the proportionality constant is the same for both pure components and the solution. In other words, this method works well when the two pure components of a binary mixture have similar pure densities. The solution density is calculated in terms of mass fraction from Eq. (48).

$$\rho = m_r \rho_r + m_o \rho_o \tag{48}$$

The second method relies on the assumption that the component volumes are additive. This assumption is valid for ideal solutions and completely immiscible, non-reacting mixtures. Again using mass fractions, the solution density is determined by Eq. (49).

$$\frac{1}{\rho} = \frac{m_r}{\rho_r} + \frac{m_o}{\rho_o} \tag{49}$$

Percent relative deviations for the two methods are shown in Figure 18, evaluated with the R1234ze(E)/RL68H liquid density data.

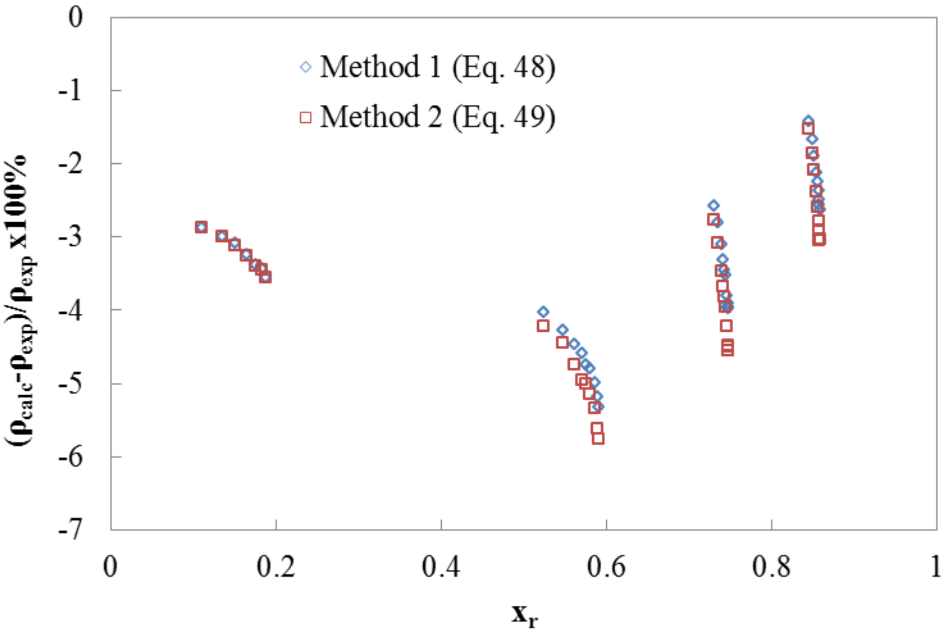


Figure 18: Relative deviations of liquid density predictions for R-1234ze(E)/RL68H

The associated statistical parameters are listed in Table 12, where density has been substituted for pressure in Equations (44-46).

Table 12: Statistical parameters for ideal solution density predictions for R-1234ze(E)/RL68H

Statistical Parameter	Method 1 (Eq. 48)	Method 2 (Eq. 49)
%AAD	3.414	3.705
%RMS	0.593	0.6421
%BIAS	-3.414	-3.705

Both methods appear to work well for R-1234ze(E)/RL68H, with RMS values of less than 0.65% and maximum deviations less than 6%. The density predictions have a negative bias which can be explained by the excess volume of mixing not accounted for in the equations. The predicted densities still agree very well with experimental data for R-1234ze(E)/RL68H.

The performance difference of the two methods for predicting density is negligible. Nevertheless, it is useful to compare the density of the pure components for similarity, as assumed by the first method. The reported density of RL68H is 977 kg/m^3 at 15°C; the liquid density of pure R-1234ze(E) at 15°C is 1195 kg/m^3. The density of the refrigerant is about 20% larger than that of the oil.

5.4 Generality Considerations

Cross comparisons of refrigerant/lubricant data and mixture model performance is difficult for the following reasons: limited information for pure lubricants; non-uniform methods for reporting VLE data; limited VLE data; and inconsistent criteria selection describing mixture model performance. In order to draw generalized conclusions for refrigerant/lubricant mixture behavior, modifications are needed in data reporting methods.

Many studies provide limited to no information about the pure lubricant, and others have cited need the need for additional lubricant data [51, 60]. Commercially available lubricant can vary due to production method/CAS# and proprietary additive packages included by the manufacturer. Very limited properties are provided at one reference temperature on technical data sheets for the lubricants. Molar mass values may be obtained from the manufacturer if it is not deemed proprietary. Pure lubricant properties are needed to convert between mole fraction and mass fraction and to use group contribution methods, PR-1VDW, and other mixture models which may require knowledge of acentric factor, critical properties, and/or chemical structure. The Wilson and Heil models require temperature-dependent values for density of the pure lubricant, making the NRTL model more attractive when less is known about the oil.

Non-uniform methods for reporting VLE data further obfuscates side-by-side comparisons of refrigerant/lubricant studies. Some studies provide bulk composition data or mass fractions of refrigerant in the liquid phase without reporting a molar mass for the lubricant. Without the molar composition of the liquid phase, additional analysis cannot be accurately completed. Additional analysis and accurate comparisons are also limited when data are only presented graphically. Tabulated values should be included or provided as supplementary material when possible.

The third issue associated with refrigerant/lubricant mixture studies is the limited amount of VLE data. Understandably, temperature ranges may be limited by an experiment apparatus; however, larger temperature ranges and a full range of concentrations should be included in VLE studies. Data limited to two concentrations and two or three temperatures is insufficient for classifying mixture behavior. Expanding studies to include data for one refrigerant with multiple oils, or one lubricant with multiple refrigerants, would allow comparisons to be made regarding mixture behavior due to a particular component. The existing database for refrigerant/lubricant behavior could be made more robust by replicating a study and replacing one component.

Methods of reporting and evaluating mixture model performance are not consistent. More comprehensive comparisons of models are needed; often only one mixture model is included in a study. The inclusion of more than three methods is rare. When agreement with only one mixture model is reported, additional models cannot be evaluated without appropriate VLE data and component information. It is possible a different model could provide better agreement than that reported. Non-uniform selection of performance criteria further complicates model comparison. While most refrigerant/lubricant VLE studies evaluate models based on pressure predictions, some studies use composition predictions instead. Criteria for evaluating performance can include 2-σ, error %AAD, %ARD/BIAS, %RMS, maximum absolute deviation, etc. Selection of a single evaluation parameter does not provide a comprehensive description of model performance. For example, %RMS and 2-σ error can be small but some deviations may be large. Reporting values for multiple evaluation criteria provides a more useful description of model performance.

To summarize, researchers investigating refrigerant/lubricant mixtures should strive to report results in a more uniform and more comprehensive manner. Using pseudo-standardized reporting methods, two different studies can be easily compared. More accessible data can facilitate future discoveries and improved understanding of refrigerant/lubricant behavior, in general.

In this study, pressures calculated using Raoult's law agreed remarkably well with the mixture data. Absolute deviations were well under 10% for refrigerant mass fractions greater than 0.25. Recalling the good agreement with Raoult's law for R-1234yf/ISO VG 10, it is possible that the HFO-refrigerant family exhibits more ideal behavior with POE lubricants than older generations of refrigerants. In order to evaluate the robustness of Raoult's law for refrigerant/lubricant mixtures in general, tabulated VLE data in the open literature were compared to Raoult's law. A list of mixture components, molecular weights, and prediction performance statistics are included in Table 13.

Table 13: Analysis of Raoult's law agreement with various refrigerant/oil mixtures

Source Ref [#]	**Mixture Components**	**Raoult, all data**			**MW_o/ MW_r**	**#data point**	**x_r min**	**x_r max**	**Temp range**	**Raoult x_r > 70%**			
		%AAD	**%RMS**	**%BIAS**						**# data points omitted**	**%AAD**	**%RMS**	**%BIAS**
[79]	R22/ Castrol SW 46	79.05	22.04	-79.05	5.6	20	0.38	0.94	253-343 K	8	36.15	**13.711**	36.15
[78]	R-125/BAB32	61.128	19.364	-61.128	2.7	10	0.09	0.38	313-333 K	Omit all	*n/a*	*n/a*	*n/a*
[80]	R-32/pentraerythritol tetrapentanoate	80.45	19.323	80.45	9.1	21	0.06	0.63	303-343 K	Omit all.	*n/a*	*n/a*	*n/a*
[81]	R744/POE ISO 68	43.44	16.87	42.788	17.4	21	0.4	0.95	285-298 K	4	16.49	**5.845**	15.686
[82]	R-744/PEBE6	58.801	16.234	58.097	n/a	25	0.17	0.96	283-303 K	11	9.001	4.216	7.4
[79]	R134a/Castrol SW 46	57.53	14.72	-43.76	4.7	20	0.34	0.93	253-343 K	12	56.44	**22.05**	44.17
[78]	R-125/BAB15	58.661	14.259	-58.661	2.6	17	0.14	0.41	313-333 K	Omit all.	*n/a*	*n/a*	*n/a*
[78]	R-143a/BAB32	47.507	13.823	-47.507	3.9	12	0.11	0.53	313-333 K	Omit all.	*n/a*	*n/a*	*n/a*
[78]	R-32/BAB32	40.121	13.492	-40.121	6.3	9	0.18	0.58	313-333 K	Omit all.	*n/a*	*n/a*	*n/a*
[78]	R-143a/BAB15	42.613	11.488	-42.613	3.7	14	0.11	0.59	313-333 K	Omit all	*n/a*	*n/a*	*n/a*
[78]	R-32/BAB15	33.789	11.16	-33.789	6	10	0.14	0.63	313-333 K	Omit all	*n/a*	*n/a*	*n/a*
[78]	R-134a/BAB15	50.148	10.632	-43.046	3	23	0.12	0.58	313-353 K	Omit all.	*n/a*	*n/a*	*n/a*
[83]	R-23/PHC14	98.672	10.178	-98.672	n/a	94	0.05	0.31	278-368 K	Omit all.	*n/a*	*n/a*	*n/a*
[78]	R-134a/BAB32	52.5537	9.49	-52.537	3.2	31	0.13	0.54	313-353 K	Omit all.	*n/a*	*n/a*	*n/a*
[80]	R-125/ pentraerythritol tetrapentanoate	33.133	8.847	33.133	3.9	16	0.06	0.68	303-323 K	Omit all.	*n/a*	*n/a*	*n/a*
[38]	R22/RL68H	36.57	8.778	-35.22	8.9	49	0.65	0.99	228-360 K	9	14.649	3.663	-12.996
[80]	R-152a/ pentraerythritol tetrapentanoate	38.547	8.546	38.547	7.2	24	0.08	0.58	303-363 K	Omit all.	*n/a*	*n/a*	*n/a*
[84]	R-744/PEC4	43.19	8.542	43.06	9.5	58	0.09	0.97	243-303 K	19	13.506	2.863	13.313
[80]	R-134a/ pentraerythritol tetrapentanoate	30.95	6.574	30.944	4.6	28	0.06	0.59	303-363 K	Omit all.	*n/a*	*n/a*	*n/a*
[80]	R-143a/ pentraerythritol tetrapentanoate	11.259	2.982	0.132	5.6	21	0.04	0.62	303-343 K	Omit all.	*n/a*	*n/a*	*n/a*
[38]	R125/RL68H	11.733	2.657	-9.471	6.4	61	0.49	0.99	232-337 K	16	3.04	0.573	0.01
[85]	R-134a/DEC	5.896	2.561	5.896	1.2	6	0.15	0.54	263-298 K	Omit all.	*n/a*	*n/a*	*n/a*
[38]	R134a/RL68H	8.78	2.23	5.38	7.5	49	0.59	0.99	227-357 K	9	6.15	1.201	6.15

Table 13 continued…

Source Ref [#]	**Mixture Components**	**Raoult, all data**			**MW_o/ MW_r**	**#data point**	**x_r min**	**x_r max**	**Temp range**	**Raoult, x_r > 70%**			
		%AAD	**%RMS**	**%BIAS**						**# data points omitted**	**%AAD**	**%RMS**	**%BIAS**
[49]	R1234ze(E)/PEC6	11.58	2.081	-7.965	4.6	56	0.07	0.92	283-353 K	37	4.782	1.147	-4.782
[49]	R1234ze(E)/PEC8	11.36	1.901	-4.053	5.6	56	0.08	0.94	283-383 K	35	7.735	1.75	-7.735
[50]	R1234yf/DC-PAG Zerol HD46	11.04	1.827	-5.751	5.3*	46	0.04	0.97	283-328 K	29	10.368	2.803	-10.368
[48]	R1234ze(E)/PEC7	11.05	1.794	-5.925	5.1	64	0.07	0.94	283-353 K	43	6.12	1.281	-6.12
[39]	R32/RL68H	7.34	1.76	-2.26	14.7	37	0.68	0.99	282- 325 K	9	3.356	0.792	3.356
[55]	R600a/LAB ISO 5	8.545	1.739	1.703	3.8*	50	0.07	0.99	283-333 K	25	3.156	0.785	0.05
[48]	R1234ze(E)/PEC9	11.06	1.725	-2.622	6.1	56	0.06	0.93	283-353 K	38	9.09	2.238	-9.09
[47]	R1234ze(E)/PEC5	9.815	1.674	-7.724	4.1	72	0.07	0.92	238-353 K	44	2.659	0.517	-2.659
[85]	R-134a/DMC	3.364	1.669	-0.06	0.9	6	0.11	0.31	278-308 K	Omit all	*n/a*	*n/a*	*n/a*
[50]	R1234yf/PAG Breox RLF-46-EP	9.937	1.427	-5.58	5.9*	63	0.05	0.97	258-338 K	37	9.856	2.142	-9.856
[46]	R1234yf/POE ISO VG 10	6.43	1.31	-5.47	n/a				286-353 K	*n/a*	*n/a*	*n/a*	*n/a*
[46]	R134a/POE ISO VG 10	5.25	1	0.29	n/a				286-353 K	*n/a*	*n/a*	*n/a*	*n/a*
[86]	R-134a/POE ISO32	1.969	0.886	1.557	5.3	12	0.96	0.98	280-355K	0	1.969	0.886	1.557
this study	R1234ze(E)/RL68H	3.551	0.884	-0.346	6.7	44	0.45	0.98	268-333 K	8	1.856	0.375	-1.676
[55]	R600a/POE ISO 7	4.98	0.82	-0.79	0				296-353 K	*n/a*	*n/a*	*n/a*	*n/a*
[87]	R134a/PAG TriEGDME	1.994	0.286	1.994	1.7	120	0.63	0.99	283-323 K	2	1.818	0.25	1.818

**Molar mass of oil was estimated by optimizing Raoult's law for minimum RMS when mass fractions were reported without lubricant information.*

For studies including an ISO 68 POE, the molar mass of the refrigerant was assumed to be the same as RL68H. When no molar mass was reported for the lubricant, the molar mass was estimated by optimizing the %RMS for the dataset. Results invoking this estimation represent the best case scenario for agreement with Raoult's law for the mixture. Studies that provided only graphical representations of data were not included due to increased uncertainty in data interpretation. The performance of Raoult's law with the data provided in the studies included in Table 13 is shown in Figure 19 in terms of %RMS and molar mass ratio.

In Figure 19, molar mass ratios of zero correspond to studies where no value was reported for the pure lubricant and concentration mass fractions were not provided to allow estimation by optimizing the performance of Raoult's law. As seen from the figure, there is no apparent correlation between the performance of Raoult's law and the molar mass ratio of the mixture.

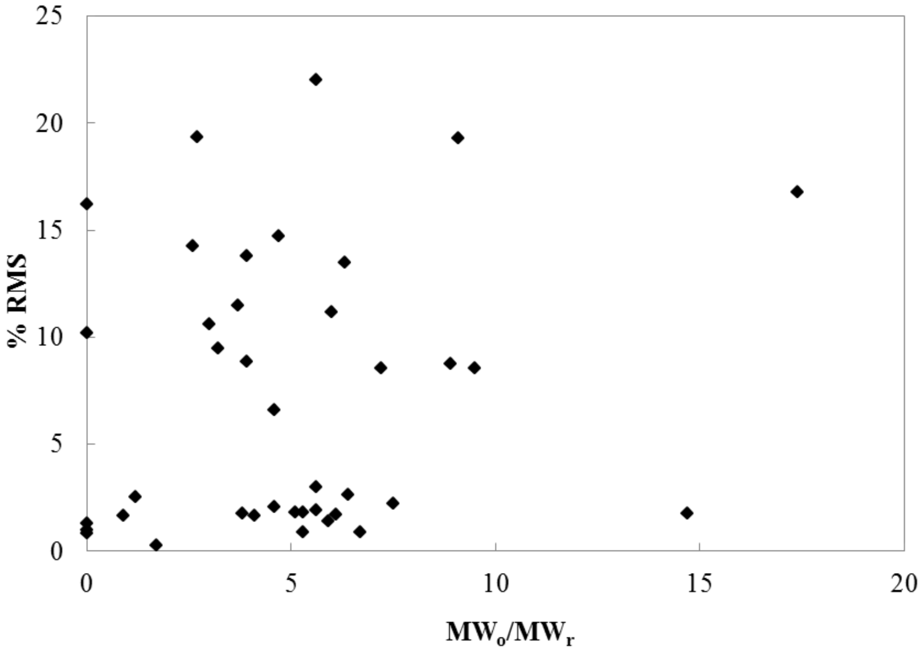


Figure 19: %RMS for Raoult's law vs molar mass ratios of mixtures in Table 13

Raoult's law did not agree as well with high pressure R-744 mixtures or mixtures containing R-22, which has one chlorine atom in the molecule. Considering the increased non-ideality of mixtures with larger lubricant concentrations, the subsets of the data containing only molar concentrations of refrigerant in the liquid greater than 70% were re-analyzed with Raoult's law. The statistical performance indicators for the subsets of data are included in the Table 13. RMS values for the data subsets are provided in Figure 20, as a function of molar mass ratio. Values for entire data sets are included for cases when all reported refrigerant concentrations were less than 70%.

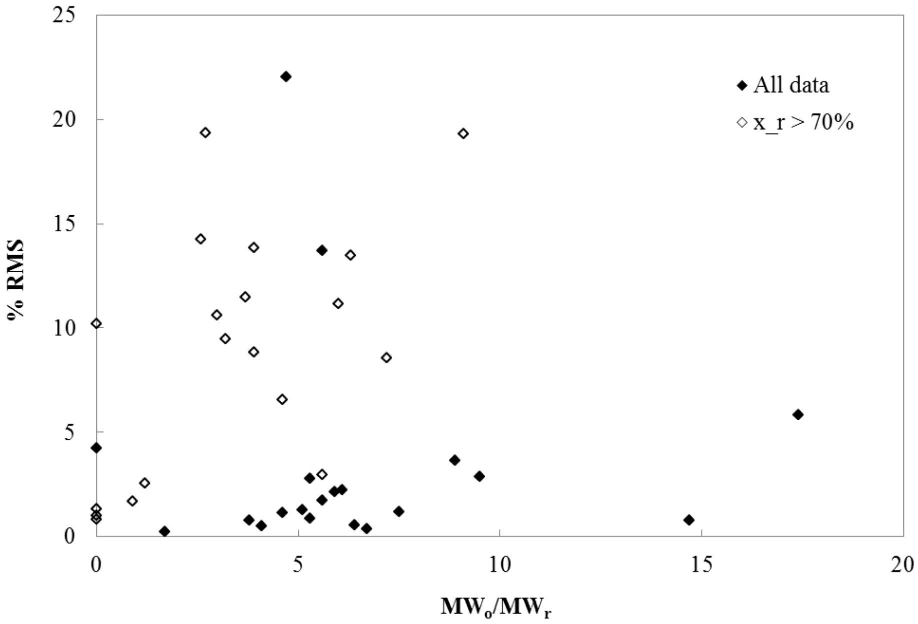


Figure 20: %RMS for Raoult's law vs molar mass ratios of mixtures in Table 13 for molar concentrations of refrigerant greater than 70%, when possible

For higher refrigerant concentrations, agreement with Raoult's law increases significantly for nearly all refrigerant/lubricant mixtures considered. Mixtures containing R-744 and R-22 continued to exhibit worse agreement, with RMS values from 2.8 to 5.9%. The data provided in Fleming (2003) [79] were supplied by the lubricant manufacturer and are deemed unfit for comparison, because a reliable evaluation of Raoult's law requires more precise pressure and molar concentration measurements than those provided by the lubricant manufacturer. A number of the studies only provided information for solutions with refrigerant molar concentrations less than 70%. These studies could therefore not be included in the second evaluation of Raoult's law. According to the results in the table, it is expected that the RMS values would improve if solutions with higher refrigerant concentrations were included.

Mixtures containing branched alkyl benzene (BAB) lubricants exhibited worse agreement with Raoult's law than did those with POE or PAG lubricants. Unfortunately, the data reported for mixtures with BAB oils were limited to lower refrigerant concentrations, preventing evaluation of Raoult's for refrigerant concentrations greater than 70%. The same is true for mixtures containing pentraerythritol tetrapentanoate lubricant. Raoult's law did agree well with mixtures containing both branched- and straight-chain POE and PAG lubricants, demonstrating improved performance at higher refrigerant concentrations.

Of the 39 refrigerant/lubricant mixtures listed in Table 13, the two taken from Ref. [79] should be omitted for precision concerns. Twenty of the remaining mixtures demonstrate good agreement with Raoult's law, having RMS values less than 5%; six mixtures are within 10% RMS. Only four of the 17 mixtures with RMS values greater than 5% contain data for molar refrigerant concentrations greater than 70%. When considering the subsets of data for these four mixtures, only one has an RMS value greater than 5% (5.85%).

Based on the results in Table 13, Raoult's law appears to agree well with mixtures containing both branched- and straight-chain PAG and POE oils. Agreement improves for higher refrigerant concentrations. Agreement is questionable for mixtures containing BAB lubricants and pentraerythritol tetrapentanoate. Raoult's law can describe mixtures containing R-744 and R-22, but generally performs better with refrigerants containing more than one hydrogen atom. These observations are limited to the refrigerants and temperature ranges listed in Table 13 and should be updated as new refrigerant/lubricant studies are published.

Molecular descriptions of the refrigerants and oils listed in Table 13 are provided in Appendix F.

Chapter 6 – Conclusions

As R-134a is phased out, new refrigerants will be selected as working fluids in air-conditioning and refrigeration systems. This thesis provides information for engineers working with such systems in terms of raw data and fitted mixture models. Mixture model performance is compared for the mixtures R-134a/RL68H and R-1234ze(E)/RL68H and investigated for sensitivity to optimized parameter values.

The present study expanded the saturated property database for the alternative refrigerant R-1234ze(E) and provided novel refrigerant/oil mixture data for mixtures of a LGWP refrigerant and polyol ester lubricant. Activity coefficients were calculated for five concentrations of the binary mixture R-1234ze(E)/RL68H and temperatures ranging from -5°C to 60°C. P-T-x-ρ data were provided for all mixtures.

VLE behavior and model results for R-1234ze(E)/RL68H were compared to data for R-134a/RL68H. Both mixtures were completely miscible for the temperatures and concentrations considered. R-1234ze(E)/RL68H mixtures had slightly lower saturation pressures than did the R-134a/RL68H mixtures, as expected from the difference in pure refrigerant saturation pressures and reported increased solubility of HFO-refrigerants in POE oils. No abnormal behavior was noted for R-1234ze(E)/RL68H mixtures, indicating that existing mixture models will not require modifications to successfully predict VLE behavior of this new family of refrigerants.

Analysis of the vapor-liquid equilibria data led to a comparison of Raoult's law and four local-composition mixture models employing the Peng-Robinson equation of state. Pressure predictions from the UNIQUAC model showed the worst agreement, having an

RMS deviation of 1.75% in pressure predictions. The Wilson and NRTL models had similar agreement, with absolute average deviations less than 4% and RMS values of 1.01 and 0.80%, respectively. Raoult's law had similar values of 3.55% AAD and 0.88% RMS, requiring no adjustable parameters and significantly less computation. The Heil model outperformed the others with an RMS of 0.445% and1.97% AAD. Maximum deviations for all models were between 10 and 30%.

Excluding UNIQUAC, the models demonstrated improved agreement at higher refrigerant concentrations. Omitting the mixtures with bulk refrigerant concentrations of 20% by mass, the RMS values for Wilson, NRTL, Heil, and Raoult's law are 0.34%, 0.28%, 0.38%, respectively. The NRTL model performs slightly better than does the Heil model when the lowest refrigerant concentration is omitted, but the four methods demonstrate comparable agreement.

Recommendations are outlined for reporting refrigerant/lubricant mixture properties. Studies should report at least the molar mass of the pure lubricant, any additional known properties, such as temperature-dependent density values, are beneficial. Results for more than one (suggested three) mixture model should be provided in terms of %RMS and %AAD statistics, at a minimum. Additional information describing model performance such as %Bias and maximum deviation provide added value. Reporting data in tabular form is advised for precise interpretation, which is hindered by providing only graphical representations of data. Expanded studies of multiple binary mixtures, keeping one component constant, are also recommended to improve the robustness of the existing refrigerant/lubricant property database from which generalizations may be made. In general, reporting methods should be more uniform and provide information in a comprehensive and accurate manner.

The R-1234ze(E)/RL68H mixtures behaved similarly to the R-134a/RL68H mixtures described in an earlier study. Trends in the mixture data followed trends present in the pure refrigerant data. Mixtures with R-1234ze(E) had a lower saturation pressure than did mixtures with R-134a, much like the difference in saturation pressure of the pure refrigerants. Molecular differences such as the presence of an additional carbon atom and carbon double-bond in R-1234ze(E) did not produce new trends in refrigerant/oil behavior that would indicate a need for new mixture models.

This work demonstrates that R-1234ze(E)/RL68H mixtures exhibit the behavior of a nearly ideal solution. Activity coefficients for bulk refrigerant concentrations less than 25% displayed less ideal behavior and greater deviations from Raoult's law; however, the RMS value for all mixtures was less than 0.9%. Raoult's law agrees within 2.5% RMS for the limited data reported for HFO-refrigerant/POE and HFO-refrigerant/PAG mixtures in the literature, indicating that HFO refrigerants like R-1234ze(E) and R-1234yf can be described as ideal solutions when mixed with POE and PAG lubricants for temperatures near the range -20 to 80°C. Reported data include molar concentrations of refrigerant from 6 to 99% in the liquid phase, demonstrating validity for nearly the entire concentration range.

Further analysis of Raoult's law was conducted using reported data for various refrigerant/lubricant mixtures and concentration ranges. Agreement with Raoult's law had no apparent correlation to molecular weight ratios; agreement improved when mixtures with lower refrigerant concentrations were omitted. Raoult's law demonstrated worse agreement with mixtures containing a branched alkyl benzene lubricant or pentraerythritol tetrapentanoate. Both branched- and straight-chain PAG and POE lubricants exhibited good agreement. Refrigerants with less than two hydrogen atoms, like R-744 and R-22, could agree within 5% RMS but generally exhibited less ideal behavior than the refrigerants included in Table 13. From the limited available data, HFO refrigerants mixed with PAG or POE oils can be adequately described by Raoult's law for temperatures ranging from -20 to 70°C, for molar concentrations of refrigerant greater than 5%.

Overall, the NRTL model is recommended for predicting refrigerant/lubricant mixture behavior. For mixtures of R-1234ze(E) and RL68H, the Heil model provided the best agreement when including the complete dataset; whereas, the NRTL model also demonstrated excellent agreement, with an RMS value less than 1%. The NRTL model out-performed the Heil model when the mixture with the lowest bulk refrigerant concentration (20% mass) was omitted from the analysis. Other refrigerant/lubricant studies have reported satisfactory performance of the NRTL model. The NRTL model has an added benefit that less information is required about the pure lubricant. The Heil model requires additional information regarding the liquid density of the lubricant component; however, the NRTL model only requires the molar mass of the oil, if needed, to determine molar concentration. In cases where the molar concentration of refrigerant in the liquid phase remains high (> 70%), Raoult's law can provide acceptable pressure predictions for mixtures with POE and PAG lubricants.

References

[1] EU 2006, Directive 2006/40/ec of the European parliament and of the Council, of 17 May 2006 relating to emissions from air-conditioning systems in motor vehicles and amending Council Directive 70/156/EEC, http://eurlex.europa.eu/LexUriServ/site/en/oj/2006/l_161/l_16120060614en00120018.pdf

[2] T. Leck, *et al*., "Novel reduced GWP refrigerant compositions for stationary air conditioning," *15th International Refrigeration and Air Conditioning Conference*, Paper 2505, 2014.

[3] "Automotive Air Conditioning History," *Automobile,* June 2010. (http://www.automobilemag.com/features/news/1007_automotive_air_conditoning_history/).

[4] Statistic Brain, 2014. (http://www.statisticbrain.com/cars-produced-in-the-world/).

[5] B. Palm, "Refrigerants of the future," *10th IEA Heat Pump Conference*, Tokyo, Japan. 2011.

[6] M. Youbi-Idrissi & J. Bonjour, "The effect of oil in refrigeration: current research issues and critical review of thermodynamic aspects," *International Journal of Refrigeration,* 31, pp. 165-179, 2008.

[7] AHRI Low-GWP Alternative Refrigerants Evaluation Program (http://www.ari.org/site/514/Resources/Research/AHRI-Low-GWP-Alternative-Refrigerants-Evaluation).

[8] S. F. Yana Motta, *et al.,* “Analysis of LGWP Alternatives for Small Refrigeration (Plugin) Applications,” *International Refrigeration and Air Conditioning Conference ,* Paper 2499, 2010.

[9] P. Reasor, V. Aute, & R. Radermacher, “Refrigerant R1234yf performance comparison investigation,” *International Refrigeration and Air Conditioning Conference ,* Paper 1085, 2010.

[10] B. H. Minor, C. Montoya, & F. S. Kasa, “HFO-1234yf performance in a beverage cooler,” *International Refrigeration and Air Conditioning Conference ,* Paper 1116, 2010.

[11] K. Endoh, H. Matsushima, & S. Takaku, “Evaluation of cycle performance of room air conditioner using HFO1234yf as refrigerant,” *International Refrigeration and Air Conditioning Conference ,* Paper 1050, 2010.

[12] A. J. Grebenkov, *et al.,* “Physical properties and equation of state for trans-1,3,3,3-tetrafluoropropene,” *Proceedings of Third IIR Conference on Thermophysical Poperties and Transfer Processes of Refrigerants,* Boulder, CO, USA. 2009.

[13] J. S. Brown, *et al.,* “Thermodynamic properties of eight fluorinated olefins,” *International Journal of Refrigeration,* 33, pp. 235-241, 2010.

[14] Y. Higashi, *et al*., “Critical parameters and saturated densities in the critical region for trans-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)),” *Journal of Chemical & Engineering Data*, 55(4), pp. 1594–1597, 2009. doi:10.1021/je900696z.

[15] K. Yamaya, *et al.* “Isochoric Specific heat capacity of trans-1,3,3,3-tetrafluorpropene (HFO-1234ze(E)) and the HFO-1234ze(E) +CO2 mixture in the liquid phase,” *Journal of Chemical & Engineering Data,* 56, pp. 1535-1539, 2011.

[16] K. Tanaka, *et al*., "Measurements of the vapor pressures and prT properties for trans-1,3,3,3- tetrafluoropropene (HFO-1234ze(E))," *Journal of Chemical Engineering Data*, 55, pp.2169-2172, 2010a. doi:10. 1021/je900756g.

[17] K. Tanaka, *et al*., "Measurements of the isobaric specific heat capacities for trans-1,3,3,3- tetrafluoropropene (HFO-1234ze(E)) in the liquid phase," *Journal of Chemical & Engineering Data,* 55, pp. 901-903, 2010b. doi:10.1021/je900799e.

[18] Klomfar *et al.,* "Isochoric P-rho-T measurements for trans-1,3,3,3-tetrafluorpropene [R-1234ze(E)] and Trifluoroiodomethane (R13I1) at Temperatures from (205 to 353) K under Pressures up to 40 MPa," *Journal of Chemical & Engineering Data,* 57(11), pp. 3270-3277, 2012.

[19] M. J. O. McLinden *et al.*, "Thermodynamic properties of trans-1,3,3,3-tetrafluoropropene [R1234ze(E)]: measurements of density and vapor pressure and a comprehensive equation of state," *International Refrigeration and Air Conditioning Conference,* Paper 1041, 2010.

[20] Y. Higashi, "Thermophysical properties of HFO-1234yf and HFO-1234ze(E)," *Symposium on Next-generation Air Conditioning and Refrigeration Technology*, Tokyo, Japan. 2010.

[21] G. Di Nicola, *et al*., "Saturated pressure measurements of trans-1,3,3,3-tetrafluoropropene (R1234ze(E)) for reduced temperatures ranging from 0.58 to 0.92," *Journal of Chemical & Engineering Data,* 57(8) pp. 2197–202, 2012.

[22] R. A. Perkins & M. L. Huber, "Measurement and correlation of the thermal conductivity of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) and trans-

1,3,3,3=tetrafluoropropene (R1234ze(E)),” *Journal of Chemical & Engineering Data,* 56, pp. 4868-4874, 2011.

[23] D. S. Cousins & A. Laesecke, “Sealed gravitational capillary viscometry of dimethyl ether and two next-generation alternative refrigerants,” *Journal of Research of NIST,* 117, pp. 231-255, 2012.

[24] J. S. Brown *et al.,* “Thermophysical properties and heat transfer and pressure drop performance potentials of hydrofluoro-olefins, hydrochlorofluoro-olefins, and their blends,” *HVAC&R Research*, 20(2), pp. 203-220, 2014.

[25] R. Akasaka, “An application of the extended corresponding states model to thermodynamic property calculations for trans-1,3,3,3-tetrafluoropropene (HFO-1234ze(E))}," *International Journal of Refrigeration,* 33, pp. 907-914, 2010.

[26] R. Akasaka, “New fundamental equations of state with a common functional form for 2,3,3,3-tetrafluoropropene (R-1234yf) and trans-1,3,3,3-tetrafluoropropene (R-1234ze(E)),” *International Journal of Thermophysics*, 32, pp. 1125-1147, 2011.

[27] E. W. Lemmon, *et al.,* NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.0, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, 2010.

[28] M. O. Mclinden, *et al*., “An extended corresponding states model for the thermal conductivity of refrigerants and refrigerant mixtures,” *International Journal of Refrigeration,* 23, pp. 43-63, 2000.

[29] S. A. Klein, *et al*., "An improved extended corresponding states method for estimation of viscosity of pure refrigerants and mixtures," *International Journal of Refrigeration,* 20(3), pp. 208-217, 1997.

[30] G. Raabe, "Molecular modeling of fluoropropene refrigerants," *Journal of Physical Chemistry B,* 116, pp. 5744-5751, 2012.

[31] G. Raabe, "Molecular dynamics studies on liquid-phase dynamics and structures of four different fluoropropenes and their binary mixtures with R-32 and CO_2," *The Journal of Physical Chemistry B,* 118, pp. 240-254, 2014.

[32] X. Dong *et al.,* "Vapor-liquid equilibria of the trans-1,3,3,3-tetrafluoropropene (R1234ze(E)) + Isobutane (R600a) system at various temperatures from (258.15 to 288.15) K," *Journal of Chemical & Engineering Data,* 57(2), pp. 541-544, 2012.

[33] K. N. Marsh & M. E. Kandil, "Review of thermodynamic properties of refrigerants + lubricant oils," *Fluid Phase Equilibria,* 199, pp. 319-334, 2002.

[34] R. Tesser, *et al.,* "Description of the vapor-liquid equilibrium in binary refrigerant/lubricating oil systems by means of an extended Flory-Huggins model," *Journal of Fluorine Chemistry,* 99, pp. 29-36, 1999.

[35] R. Tesser, *et al.,*"Vapour-liquid equilibrium measurements for binary mixtures of R32, R143a, R134a and R125 with a perfluoropolyether lubricant," *Journal of Fluorine Chemistry,* 121, pp. 15-22, 2003.

[36] R. Tesser, *et al.,* "Phase equilibria in binary mixtures refrigerant + fluorinated lubricating oil: vapor-liquid and liquid-liquid measurements," *Journal of Chemical & Engineering Data,* 49, pp. 838-846, 2004.

[37] Y. Xu, *et al.*, “Experimental Data and Description of the Phase Equilibrium in the Binary system of Ethyl Fluoride and Polyol Ester Oil (Planetelf ACD 32),” *Journal of Chemical & Engineering Data,* 58(8), pp. 2311-2315, 2013.

[38] W. L. Martz, “Refrigerant-oil mixtures and local composition modeling,” *MS Thesis*, University of Illinois, Urbana-Champaign, 1994.

[39] C. M. Burton, “Vapor-liquid equilibria for R-32 and R-410A mixed with a polyol ester: non-ideality and local composition modeling,” *MS Thesis*, University of Illinois, Urbana-Champaign, 1997.

[40] M. A. Marcelino Neto & J. R. Barbosa, “Solubility, density and viscosity of a mixture of R-600a and polyol ester oil,” *International Journal of Refrigeration*, 31, pp. 34-44, 2008.

[41] J. J. Grebner & R. R. Crawford, “Measurement of pressure-temperature-concentration relations for mixtures of R-12/mineral oil and R-134a synthetic oil,” *ASHRAE Transactions 99 (part 1),* 1993.

[42] X. H. Han, *et al*., “Solubility and miscibility for the mixture of (ethyl fluoride + polyol ester oil),” *Journal of Chemical & Engineering Data,* 55(9), pp. 3200-3207, 2010.

[43] N. Elvassore, *et al.,* “A cubic equation of state with group contributions for the calculation of vapor-liquid equilibria of mixtures of hydrofluorocarbons and lubricant oils,” *Industrial & Engineering Chemical Research,* 38, pp. 2110-2118, 1999.

[44] A. Bertucco, *et al.,* “A perturbed-hard-sphere-chain equation of state for phase equilibria of mixtures containing a refrigerant and a lubricant oil,” *Fluid Phase Equilibria,* 158-160, pp. 183-191, 1999.

[45] J. F. Heil & J. M. Prausnitz, “Phase equilibria in polymer solutions,” *American Institute of Chemical Engineers Journal,* 12(4), pp. 678-685, 1966

[46] M. A. Marcelino Neto, R. M. Franca, & J. R. Barbosa Jr., “Convection-driven absorption of R-1234yf in lubricating oil,” *International Journal of Refrigeration,* 44, pp. 151-160, 2014.

[47] Y. Sun, X. Wang, & N. Gong, “Solubility of trans-1,3,3,3,-tetrafluoroprop-1-ene (R1234ze(E)) in pentaerythritol tetrapentanoate (PEC5) in the temperature range from 283.15 to 353.15 K,” *International Journal of Refrigeration,* 48, pp. 114-120, 2014.

[48] Y. Sun, X. Wang, & N. Gong, “Solubility of trans-1,3,3,3-tetrafluoropropene (R1234ze(E)) in pentaerythritol ester heptanoic acid (PEC7) and in pentaerythritol tetranonanoate (PEC9) between 283.15K and 353.15K, *Fluid Phase Equilibria,* 387, pp. 154-159, 2015.

[49] X. Wang, Y. Sun, & K. Kang, “Experimental investigation for the solubility of R1234ze(E) in pentaerythritol tetrahexanoate and pentaerythritol tetraoctanoate,” *Fluid Phase Equilibria*, 400, pp. 38-42, 2015.

[50] S. Bobbo, C. Zilio, M. Scattolini, & L. Fedele, “R1234yf as a substitute of R134a in automotive air conditioning. Solubility measurements in two commercial PAG oils,” *International Journal of Refrigeration,* 40, pp. 302-308, 2014.

[51] A. W. Islam & M. H. Rahman, “A Review of Barker’s activity coefficient method and VLE data reduction,” *Journal of Chemical Thermodynamics,* 44, pp. 31-37, 2012.

[52] H. Orbey & S. I. Sandler, *Modeling Vapor-Liquid Equilibria: cubic equations of state and their mixing rules*. Cambridge University Press, 1998.

[53] M. R. Conde, “Estimation of thermophysical properties of lubricating oils and their solutions with refrigerants: an appraisal of existing methods,” *Applied Thermal Engineering,* 16(1), pp. 51-61, 1996.

[54] A. Restrepo, G. D. Bent, & H. H. Michels, “Solution theory model for thermophysical properties of refrigerant/lubricant mixtures,” *American Institute of Chemical Engineers Journal,* 55(12), pp. 3241-3247, 2009.

[55] M. A. Marcelino Neto & J. R. Barbosa Jr., “A departure-function approach to calculate thermodynamic properties of refrigerant-oil mixtures,” *International Journal of Refrigeration,* 36, pp. 972-979, 2013.

[56] J.-N.Jaubert & F. Mutelet, “VLE predictions with the Peng-Robinson equation of state and temperature dependent kij calculated through a group contribution method,” *Fluid Phase Equilibria,* 224, pp. 285-304, 2004.

[57] C.-A.Hwang, J. C. Holste, K. R. Hall, & G. A. Mansoori, “A simple relation to predict or correlate the excess functions of multicomponent mixtures,” *Fluid Phase Equilibria*, 62, pp. 173-189, 1991.

[58] S.-E. K. Fateen, M. M. Khalil, & A. O. Elnabawy, “Semi-empirical correlation for binary interaction parameters of the Reng-Robinson equation of state with the van der Waals mixing rules for the prediction of high-pressure vapor-liquid equilibrium,” *Journal of Advanced Research,* 4(2), pp.137-145, 2013.

[59] A. Yokozeki, “Solubility correlation and phase behaviors of carbon dioxide and lubricant oil mixtures,” *Applied Energy,* 84(2), pp. 159-175, 2007.

[60] S. E. Quinones-Cisneros, J. Garcia, J. Fernandez, & M. A. Monsalvo, "Phase and viscosity behavior of refrigerant-lubricant mixtures," *International Journal of Refrigeration,* 28, pp. 714-724, 2005.

[61] S. Bobbo, L. Fedele, & R. Stryjek, "Oil structure influence on the solubility of carbon dioxide in POE lubricants," *International Refrigeration and Air Conditioning Conference,* Paper 776, 2006.

[62] G.M. Wilson, "A new expression for the excess free energy of mixing," *Journal of Americal Chemical Society,* 86(2), pp. 127-130, 1964.

[63] H. Renon & J. M. Prausnitz, "Local compositions in thermodynamic excess functions for liquid mixtures," *American Institute of Chemical Engineers Journal,* 14(1), pp. 135-144, 1968.

[64] D. S. Abrams & J. M. Prausnitz, "Statistical thermodynamics of liquid mixtures," *American Institute of Chemical Engineers Journal,* 21(1), pp. 116-128, 1975.

[65] D. Y. Peng & D. B. Robinson, "A new two-constant equation of state," *Industrial & Engineering Chemistry Process Design and Development,* 15(1), pp. 59-64, 1976.

[66] R. J. Beattie & J. A. Karnaz, "Investigation of low GWP refrigerant interaction with various lubricant candidates," *International Refrigeration and Air Conditioning Conference,* Paper 1123, 2012.

[67] H. O. Spauchus, "Thermodynamic properties of refrigerant-oil solutions, Part 1," *ASHRAE Journal,* August, pp. 47-52, 1963.

[68] M. Moshfeghian, A. Shariat, & R. N. Maddox, "Prediction of refrigerant thermodynamic properties by equations of state: VLE of binary mixtures," *Fluid Phase Equilibria,* 80, pp. 33-44.

[69] H. O. Spauchus, "Thermodynamic properties of refrigerant-oil solutions, Part 2," *ASHRAE Journal,* August, pp. 63-71, 1963.

[70] G. Scatchard & G. M. Wilson, "Vapor-liquid equilibrium. XIII. The system water-butyl glycol from 5 to 85," *Journal of American Chemical Society,* 86(2), pp133-137, 1964.

[71] J. M. Marina & D. P. Tassios, "Prediction of ternary liquid-liquid equilibrium from binary data," *Industrial Engineering and Chemistry Process Design Development,* 12, pp. 271-274, 1973.

[72] M. R. Gennero de Chialvo & A. C. Chialvo, "Determination of the function F(H^E, G^E)=0 for Wilson, NRTL, LEMF, and UNIQUAC equations," *Industrial Engineering Chemistry Research,* 12, pp. 1035-1039, 1994.

[73] U. Hesse & H. Kruse, "Prediction of the behavior of oil refrigerant mixtures," *International Refrigeration and Air Conditioning Conference*, Paper 76, 1988.

[74] T. Tsuboka & T. Katayama, "Modified Wilson equation for vapor-liquid and liquid-liquid equilibria," *Journal of Chemical Engineering of Japan,* 8(3), pp. 181-186, 1975.

[75] W. Wang & K. C. Chao, "The complete local concentration models activity coefficients," *Chemical Engineering Science,* 38(9), pp. 1483-1492, 1983.

[76] N. Silverman & D. Tassios, "Prediction for multicomponent vapor-liquid equilibrium with the Wilson equation," *Industrial Engineering and Chemistry Process Design Development,* 23(1), pp. 586-589, 1984.

[77] R. Tillner-Roth & H. D. Baehr, "An international standard formulation for the thermodynamic properties of 1,1,1,2-tetrafluorethane (HFC-134a) for temperatures from 170 K to 455 K and pressures up to 70 MPa," *Journal of Physical Chemistry, Reference Data,* 23(5), pp. 657-729, 1994.

[78] K. Takigawa, S. I. Sandler, & A. Yokozeki, "Solubility and viscosity of refrigerant/lubricant mixtures:hydrofluorocarbon/alkylbenzene systems," *International Journal of Refrigeration,* 25(8), pp. 1014-1024, 2002.

[79] J. S. Fleming & Y. Yan, "The prediction of vapour-liquid equilibrium behavior of HFC blend-oil mixtures from commonly available data," *International Journal of Refrigeration,* 26, pp. 266-274, 2003.

[80] A. Wahlstrom & L. Vamling, "Solubility of HFC32, HFC125, HFC134a, HFC143a, and HFC152a in a pentaerythritol tetrapentanoate ester," *Journal of Chemical and Engineering Data,* 44(4), pp. 823-828, 1999.

[81] M. A. Marcelino Neto & J. R. Barbosa Jr., "Phase and volumetric behavior of mixtures of carbon dioxide(R-744) and synthetic lubricant oils," *Journal of Supercritical Fluids,* 50(1), pp. 6-12, 2009.

[82] L. Fedele, S. Bobbo, M. Scattolini, & R. Stryjek, "Solubility measurements and data correlation of carbon dioxide in pentaerythritol tetra(2-ethylbutanoate) (PEBE6)," *Journal of Chemical and Engineering Data,* 56(1), pp. 62-64, 2011.

[83] C. Bogatu, *et al.,* "Fluid phase equilibria in the binary system trifluoromethane+1-phenyloctane," *Fluid Phase Equilibria,* 295(2), pp. 186-193, 2010.

[84] F. Pernechele, S. Bobbo, L. Fedele, & R. Stryjek, "Solubility of carbon dioxide in pentaerythritol tetrabutyrate (PEC4) and comparison with other linear chained pentaerythritol tetraalkyl esters," *International Journal of Thermophysics,* 30(4), pp. 1144-1154, 2009.

[85] E. R. Lopez, A. M. Mainar, J. S. Urieta, & J. Fernandez, “Solubility of HFC134a (1,1,1,2-tetrafluoroethane) in two dialkyl carbonates,” *Journal of Chemical and Engineering Data,* 54(9), pp. 2609-2615, 2009.

[86] M. L. Huber, C. D. Holcomb, S. L. Outcalt, J. R. Elliott, “Vapor-liquid equilibria for an R134a/lubricant mixture: measurements and equation-of-state modeling,” *2000 ASHRAE Winter Meeting,* 2000.

[87] P. Marchi, G. Scalabrin, E. C. Ihmels, K. Fischer, & J. Gmehling, “Bubble pressure measurements for the (1,1,1,2-tetrafluoroethane +triethylene glycol dimethyl ether(system,” *Journal of Chemical Thermodynamics,* 38, pp. 1247-1253, 2006.

Appendix A: VLE Data

Table A.1: Saturated liquid density data and uncertainty for pure R-1234ze(E)

T [K]	ΔT [K]	ρ [kg/m³]	Δρ [kg/m³]
335.9561	0.053563	1018.179	0.514547
335.1632	0.05204	1021.614	0.521138
337.2377	0.052699	1012.376	0.513179
338.8833	0.055498	1004.871	0.519321
331.0308	0.054816	1039.448	0.52066
333.0537	0.05265	1030.797	0.520491
323.7303	0.050516	1069.145	0.511052
325.8911	0.049995	1060.621	0.524662
328.6272	0.050571	1049.462	0.519631
329.29	0.052396	1046.769	0.517584
311.508	0.052377	1114.855	0.523884
314.3974	0.052751	1104.511	0.514477
316.6992	0.051404	1096.031	0.521629
318.3876	0.051371	1089.74	0.506178
320.3792	0.054124	1082.164	0.524598
322.3051	0.055224	1074.723	0.515333
298.1987	0.050833	1160.84	0.517457

305.6979	0.052802	1135.448	0.520554
306.3631	0.055379	1133.172	0.50884
300.7764	0.055112	1151.802	0.521466
303.0608	0.05318	1144.431	0.522509
305.0465	0.054191	1137.669	0.523981
306.8502	0.054625	1131.428	0.521079
309.6837	0.052627	1121.485	0.517829
311.3909	0.054767	1115.361	0.515382
284.088	0.054617	1206.415	0.516453
282.5264	0.053774	1211.356	0.520596
282.3549	0.051493	1211.881	0.523321
281.7325	0.051326	1213.846	0.52356
281.4477	0.052125	1214.702	0.517864
279.252	0.049778	1221.493	0.523652
279.1268	0.050683	1221.846	0.520445
277.5331	0.051901	1226.71	0.503896
277.4104	0.053393	1227.066	0.523167
275.8985	0.051254	1231.72	0.514063
274.4594	0.051046	1236.109	0.517887
274.3312	0.050652	1236.46	0.509681
274.2812	0.052246	1236.636	0.520889
295.4848	0.053096	1169.944	0.512752

296.075	0.051047	1168.022	0.517352
296.6611	0.051547	1166.076	0.523726
297.6442	0.051454	1162.787	0.522349
283.6269	0.052301	1207.78	0.521782
269.5317	0.060521	1250.644	0.531537
289.2894	0.052561	1190.067	0.520573
290.274	0.051644	1186.782	0.52372
288.579	0.054316	1192.227	0.51189
286.8562	0.053946	1197.699	0.52257
286.8287	0.05633	1197.767	0.509751
286.7255	0.053625	1198.073	0.513624
285.1433	0.051575	1203.066	0.51244
335.1658	0.051718	1021.601	0.519564
337.2165	0.052126	1012.469	0.516042
338.8751	0.053283	1004.885	0.522177
293.9223	0.052449	1174.934	0.511843
292.6595	0.054349	1178.998	0.521227
292.648	0.053229	1179.02	0.524049
292.2978	0.050398	1180.147	0.522583
272.9726	0.051032	1240.255	0.523345
272.9788	0.053024	1240.245	0.520352
271.9562	0.05135	1243.314	0.540242

271.8073	0.05144	1243.761	0.547859
271.7975	0.05293	1243.785	0.539167
271.7993	0.052713	1243.795	0.526394
271.9582	0.051693	1243.314	0.539744
270.996	0.057968	1246.295	0.527807
271.0087	0.053125	1246.262	0.525256
270.8462	0.053177	1246.758	0.522836
270.8009	0.053971	1246.889	0.521195

Table A.2: Saturated pressure data and uncertainty for pure R-1234ze(E)

T [K]	**ΔT [K]**	**P [kPa]**	**ΔP [kPa]**
336.1303	0.045057	1385.197	1.733596
335.3794	0.038986	1360.14	1.724675
337.4264	0.04103	1443.369	5.724057
339.1047	0.039355	1487.07	1.723917
331.2679	0.038412	1230.759	1.72396
333.2856	0.038758	1292.501	1.723883
323.9968	0.039932	1029.196	1.725546
326.0928	0.04103	1084.164	1.725326

328.8752	0.038209	1162.402	1.724413
329.5018	0.04016	1180.326	1.723861
311.7995	0.038209	743.5573	1.723985
314.6249	0.038209	803.9384	1.724576
316.9268	0.039355	854.4969	1.724766
318.6059	0.038551	894.3997	1.723855
320.6043	0.037552	942.4362	1.723931
322.5596	0.040622	991.4261	1.724106
298.1581	0.042624	503.3801	1.724407
305.8183	0.050963	628.2924	1.725367
306.3563	0.065132	638.2141	1.729645
301.0302	0.041338	548.4932	1.72404
301.0576	0.039715	549.038	1.724034
303.141	0.039372	581.9008	1.725759
305.1578	0.03738	616.0859	1.723914
306.9696	0.037711	648.1599	1.72393
309.8547	0.041576	703.2316	1.723833
311.5679	0.038063	736.6253	1.724901
283.2734	0.041036	311.5192	1.724192
281.5516	0.039849	293.6352	1.724514
281.337	0.038603	291.9224	1.724856
280.4996	0.0391	281.5274	1.724063

280.2434	0.039776	279.2397	1.723969
277.8165	0.04103	256.5805	1.724244
277.7282	0.041914	255.89	1.724179
276.0044	0.04242	240.8917	1.72429
275.8745	0.045411	240.0124	1.724411
274.1218	0.047981	225.3805	1.724355
272.4597	0.046398	212.1238	1.723994
272.316	0.042057	211.2047	1.724115
272.2652	0.045572	210.8782	1.724143
295.2437	0.070072	459.4042	1.727749
295.8385	0.060681	467.7359	1.725945
296.4933	0.05758	477.2204	1.72635
297.4691	0.053913	491.5699	1.725864
282.7455	0.038435	301.7876	1.723982
288.6546	0.037552	368.4243	1.724013
289.8771	0.038487	384.8511	1.724014
288.0587	0.038603	362.2217	1.724601
286.4006	0.046187	342.6504	1.729868
286.1976	0.039327	340.7201	1.724952
286.1092	0.039999	339.9106	1.724367
284.3924	0.042205	320.7205	1.725218
293.7257	0.039372	438.1223	1.724307

292.4326	0.0391	420.2951	1.723892
292.082	0.040573	415.5703	1.723986
271.2149	0.050723	202.8582	1.724456
271.1934	0.051263	202.9541	1.725596
269.9	0.049665	193.3511	1.726434
269.7976	0.050946	192.978	1.725399
268.6881	0.048807	184.9922	1.724773
268.4656	0.043142	183.7752	1.724673
268.4504	0.046057	183.782	1.724336

Table A.3: VLE data and uncertainty for R-1234ze(E)/RL68H mixtures

$(x_r)_{mix}$	T [K]	P [kPa]	ρ [kg/m³]	ΔT [K]	ΔP [kPa]	Δρ [kg/m³]
1	333.2856	1292.501	1029.685	0.038758	1.723883	0.520491
1	323.9968	1029.196	1067.89	0.039932	1.725546	0.511052
1	314.6249	803.9384	1103.676	0.038209	1.724576	0.514477
1	303.141	581.9008	1144.378	0.039372	1.725759	0.522509
1	298.1581	503.3801	1161.146	0.042624	1.724407	0.517457
1	292.4326	420.2951	1179.865	0.0391	1.723892	0.524049
1	283.2734	311.5192	1208.829	0.041036	1.724192	0.516453
1	272.316	211.2047	1242.393	0.042057	1.724115	0.509681
1	268.4504	183.782	1254.071	0.046057	1.724336	0.521195
0.860441	333.8257	1289.259	1047.37	0.043986	1.765158	0.508022
0.860441	323.1133	984.3897	1077.167	0.04436	1.783173	0.520492
0.860441	312.8314	741.2151	1105.004	0.038644	1.734695	0.514845
0.860441	303.1297	569.629	1130.584	0.039664	1.741101	0.509877
0.860441	292.2014	407.8087	1158.6	0.038325	1.75146	0.519911
0.860441	282.3479	294.1054	1183.138	0.041484	1.750272	0.521459
0.860441	272.925	208.7879	1205.96	0.043755	1.809703	0.521877
0.860441	269.6574	185.5432	1213.728	0.047309	1.761302	0.523127
0.860441	267.1167	168.5116	1219.715	0.041821	1.733086	0.505965
0.600204	333.6454	1210.226	1035.972	0.03977	1.741925	0.518838

0.600204	322.7148	923.4734	1054.833	0.044022	1.75223	0.517273
0.600204	312.3035	697.3127	1072.659	0.038733	1.801277	0.520198
0.600204	303.5168	543.4292	1087.596	0.038087	1.731522	0.522421
0.600204	298.1554	464.198	1096.663	0.042144	1.747279	0.522322
0.600204	292.353	385.6775	1106.435	0.04487	1.75156	0.527617
0.600204	282.2168	275.0168	1123.403	0.041799	1.769522	0.520591
0.600204	272.6529	196.0757	1139.295	0.048252	1.836196	0.519922
0.600204	269.5038	176.1719	1144.502	0.102167	1.792331	0.52168
0.750022	333.5933	1266.712	1049.293	0.039879	1.761135	0.520065
0.750022	323.6934	989.5779	1071.324	0.038357	1.741715	0.518693
0.750022	312.848	741.8734	1095.027	0.043986	1.743631	0.515583
0.750022	303.5175	569.5986	1115.057	0.040132	1.738958	0.52323
0.750022	297.3164	474.9781	1128.185	0.038141	1.774981	0.5256
0.750022	292.5002	406.9106	1138.279	0.03738	1.754507	0.521919
0.750022	282.6201	291.7988	1158.706	0.040474	1.797252	0.523264
0.750022	272.4077	203.0724	1179.427	0.049754	1.780188	0.520129
0.750022	272.3079	202.5272	1179.628	0.047422	1.773445	0.520817
0.750022	269.496	183.1227	1185.261	0.0476	1.755714	0
0.750022	269.498	183.0778	1185.257	0.050088	1.752416	0
0.20109	333.7763	629.6682	979.6185	0.056568	2.199197	0.523824
0.20109	323.0704	500.9436	990.3269	0.059179	1.899057	0.523336
0.20109	314.1058	404.5284	999.2636	0.043307	1.755424	0.515713

0.20109	303.5238	307.7888	1009.778	0.051661	1.82234	0.521064
0.20109	292.5299	222.1507	1020.661	0.040949	1.768946	1.206765
0.20109	282.6992	159.2315	1030.357	0.039327	1.836192	0.652228
0.20109	273.9649	111.333	1038.945	0.069579	1.814664	7.116987
0.20109	272.0085	108.5392	1040.865	0.039015	1.819712	0.663143
0.400104	333.5665	1044.802	1014.934	0.039234	1.746162	0.527486
0.400104	323.4765	820.5304	1026.968	0.037747	1.746499	0.538373
0.400104	313.8468	640.3309	1038.582	0.03738	1.776305	0.539728
0.400104	303.7621	485.2678	1050.878	0.040115	1.754924	0.597351
0.400104	292.738	349.6676	1064.477	0.04368	1.749789	0.726557
0.400104	282.202	248.8063	1077.626	0.038285	1.765031	11.49635
0.400104	273.0943	181.0157	1089.114	0.040275	1.786103	0.63277

Table A.4: Calculated VLE parameters for R1234ze(E)/RL68H mixtures

γ_r	$x_{r,mass}$	Pe	ϕ_r	$x_{,r}$
1.023	0.8452	0.9997	0.8005	0.9734
1.017	0.8493	0.9995	0.8312	0.9742
1.005	0.8522	0.9992	0.8596	0.9748
1.011	0.8542	0.9996	0.8814	0.9752
1.006	0.856	0.9997	0.9053	0.9755

1.001	0.8572	0.9997	0.9245	0.9758
0.9903	0.8581	0.9997	0.941	0.9759
0.9931	0.8583	0.9997	0.9457	0.976
0.9934	0.8585	0.9998	0.9494	0.976
1.084	0.5247	0.9968	0.8123	0.881
1.068	0.5471	0.9975	0.841	0.8902
1.052	0.5619	0.9979	0.8672	0.8959
1.043	0.5712	0.9983	0.8872	0.8994
1.041	0.5758	0.9986	0.8984	0.901
1.031	0.5799	0.9987	0.9105	0.9026
1.019	0.5857	0.999	0.9293	0.9046
1.015	0.5898	0.9993	0.9444	0.9061
1.024	0.591	0.9994	0.9484	0.9065
1.042	0.7306	0.9991	0.8035	0.9479
1.036	0.7354	0.9991	0.8313	0.9491
1.031	0.7392	0.9992	0.8595	0.95
1.027	0.7418	0.9994	0.8818	0.9507
1.028	0.7432	0.9995	0.8952	0.951
1.021	0.7441	0.9995	0.9058	0.9512
1.01	0.7457	0.9995	0.9253	0.9516
1.007	0.7469	0.9996	0.9423	0.9519
1.008	0.747	0.9996	0.9424	0.9519

1.011	0.7472	0.9997	0.9463	0.952
1.011	0.7472	0.9997	0.9463	0.952
1.244	0.1096	0.9738	0.9014	0.4523
1.104	0.1352	0.9806	0.9133	0.5118
1.039	0.1508	0.985	0.9238	0.5436
0.9934	0.1647	0.9891	0.9358	0.5695
0.9509	0.1754	0.9921	0.9484	0.5879
0.9097	0.1824	0.9942	0.9591	0.5995
0.8465	0.1873	0.9954	0.9688	0.6072
0.8812	0.1882	0.9959	0.9689	0.6086
1.082	0.3621	0.9903	0.8375	0.792
1.068	0.3717	0.9927	0.8595	0.7987
1.057	0.3785	0.9944	0.8797	0.8034
1.048	0.384	0.9959	0.8994	0.807
1.041	0.3886	0.9971	0.9191	0.81
1.036	0.3919	0.9979	0.936	0.8121
1.034	0.394	0.9985	0.9489	0.8135

Appendix B: Thermodynamic Relations

Vapor-liquid equilibrium can be described using thermodynamic expressions relating measurable thermophysical properties to thermodynamic concepts including Gibbs free energy, fugacity, and activity. The Gibbs free energy is defined as

$$g = h - Ts \tag{B.1}$$

where g, h, and s are the specific molar properties for Gibbs free energy, enthalpy, and entropy, respectively. Substituting the definition for enthalpy and differentiating, the change in Gibbs free energy can be expressed as

$$dg = vdP - sdT \tag{B.2}$$

and for isothermal processes:

$$dg = vdP \tag{B.3}$$

For ideal gases, equation (B.3) becomes

$$dg = RTd(\ln P) \tag{B.4}$$

However, many real fluids do not behave like ideal gases. Fugacity, *f*, is a correction term that can be substituted for pressure to account for the non-ideal vapor behavior of real gases. The expression for the change in Gibbs free energy for a real gas is

$$dg = RTd(\ln f) \tag{B.5}$$

providing a useful relation between fugacity and Gibbs free energy.

The fugacity coefficient is a more convenient way of expressing fugacity. For mixtures, the fugacity coefficient for a component, *i,* is defined by equation (B.6)

$$\Phi_i = \frac{f_i}{y_i P} \tag{B.6}$$

Where f_i is the fugacity of component *i* in the mixture, *P* is the mixture pressure, and y_i is the molar concentration of component *i* in the vapor phase. For binary refrigerant/lubricant mixtures, the mixture vapor can be safely approximated as pure refrigerant vapor ($y_r = 1$) [67].

With some mathematical manipulation and recognizing that the fugacity coefficient approaches unity for low pressures, the fugacity coefficient of component *i* in a mixture can be written as

$$d\left(\ln \Phi_i\right) = \frac{1}{RT}\left(v_i - \frac{RT}{P}\right)dP \tag{B.7}$$

and integrated to give

$$\ln \Phi_i = \frac{1}{RT}\int_0^P \left(v_i - \frac{RT}{P}\right)dP \tag{B.8}$$

Combing equation (B.8) and an equation of state, the fugacity coefficient can be expressed in terms of equation of state parameters at a prescribed temperature and pressure.

Fugacity acts as a correction term for non-ideal vapor behavior. For ideal mixtures with non-ideal vapor behavior, a modification of Raoult's law, known as the Lewis-Randall rule applies.

$$f_i^{\text{(ideal solution)}} = y_i f_i^{\text{(pure component)}} \tag{B.9}$$

Most mixtures, however, are not ideal and require an additional correction term.

The activity of a component is the ratio of the fugacity of a component in a mixture to the fugacity of the same component at a reference state. In this study, the saturation pressure was adopted as the reference state.

$$a_i = \frac{f_i}{f_i^{sat}} = \frac{f_i(T,P,x)}{f_i(T,P^{sat},x^{sat})} \quad \text{(B.10)}$$

The activity coefficient, γ_i, is then defined as

$$\gamma_i \equiv \frac{a_i}{x_i} \quad \text{B.11)}$$

where a_i is the activity of component *i* in the solution, and x_i is the mole fraction of component *i* in the liquid phase.

Non-ideal solutions with real gases can therefore be described by correcting the Lewis-Randall rule using the activity coefficient, as defined by equation (B.12)

$$\gamma_i = \frac{y_i P \Phi_i}{x_i P_{i,sat} \Phi_{i,sat} Pe} \quad \text{(B.12)}$$

The expression is a ratio of the fugacity of the refrigerant vapor in the system and the product of the molar concentration and fugacity of the refrigerant in the liquid phase. The saturated state terms are evaluated at the saturation pressure of the pure refrigerant; the Poynting effect is added as a correction term.

Mixtures with positive deviations to Raoult's law exhibit activity coefficients greater than one and correspond to mixtures with an excess Gibbs energy greater than zero. Activity coefficients greater than unity indicate that intramolecular forces are greater than intermolecular forces. Conversely, activity coefficients less than unity correspond to mixtures where intermolecular forces dominate and hydrogen bonding may be present.

Appendix C: UNIQUAC Parameters

The UNIQUAC model requires structural information for each component in a mixture. The information takes the form of a size parameter (*q*) and structure parameter (*r*), which are determined from the pure component molecules.

To determine the parameters, the molecular formula of the pure components must be known. The molecular structure can be considered a combination of common chemical groups with known molecular properties. Tables of chemical groups and their respective parameters can be found in numerous sources [C1-C3].

The size and structure parameters of components are sums of the chemical group parameters

$$r = \sum_i n_i r_i \tag{C.1}$$

$$q = \sum_i n_i q_i \tag{C.2}$$

where r_i and q_i are the contributions of the chemical groups and n_i is the number of the *i* chemical groups in the molecule.

UNIQUAC parameters for the components in this study are listed in Table C.1, where the parameters for RL68H and R-134a were taken from [38].

Table C.1: *UNIQUAC Parameters*

Molecule	**Molecular Formula**	***r***	***q***
R-1234ze(E)	$CF_3CF{=}CHF$	2.74	2.49
R-134a	CH_2CF_3F	2.46	2.36
RL68H	Estimated	29.40	24.36

Appendix C References

[C1] *A. Bondi, Physical Properties of Molecular Crystals, Liquids, and Glasses Wiley, New York, 1968.*

[C2] *C. F. Beaton & G. F. Hewitt, Physical Property Data for the Design Engineer, Hemisphere Publishing Co., New York, 1989.*

[C3] *A. Fredenslund & J. M. Sorenson, "Group Contribution Estimation Methods." Models for Thermodynamic and Phase Equilibria Calculations. Ed. S. I. Sandler. Marcel Dekker, Inc., New York, 1994.*

Appendix D: Mixture Model Codes

```
"x = mole fraction in the liquid phase"
"y = mole fraction in the vapor phase"
"! GAMMA-PHI MODEL FOR 2-COMPONENT MIXTURES"
{la1=3931.68                    “fitting parameters…minimize OBJ_final to determine”
la2=-999.08}


"--------constants------------"
MW_o=765                        {RL68H manuf}
MW=MolarMass(fluid$)
R_u=8.314
R=R_u/MW
T_c=T_crit(fluid$)
P_c=P_crit(fluid$)
vol_tot=0.003430161                   "total volume of system"
y_r=1                           "mole fraction of refg in vapor phase"
```

```
fluid$='R1234ze'


{---------PR-EOS-------------}
        a=0.45724*(R*T_c)^2/P_c
        b=0.07780*R*T_c/P_c
        kappa=0.37464+1.54226*omega-0.26992*omega^2             {PR}
        {!kappa is determined experimentally}
        omega=AcentricFactor(fluid$)
        {kappa=0.378893+1.4897153*omega-0.17131848*omega^2+0.0196554*omega^3+k1*(1+(T/Tc)^(1/2))*(0.7-T/Tc)       {PR-SV1}}


{----------constants for models--------------}
alpha_12=alpha_21
alpha_12=0.5                "NRTL for refg/oil"
n_c=10                 {UNIQUAC from Martz IJR, coordination number}
r_1=2.74               { UNIQUAC, R-1234ze}
```

```
r_2=29.4          { UNIQUAC from Martz thesis, table C2, POE     structural parameter based on chemical components}
q_r=2.49          { UNIQUAC, R-1234ze}
q_o=24.36         { UNIQUAC from Martz thesis, table C2, POE     size parameter based on chemical components}


N=44       "number of data points...rows in parametric table"


Duplicate i=1, N
{input experimental data in parametric table}
    T[i]=tablevalue('Mix1Array', i, 'T')
    P_exp[i]=tablevalue('Mix1Array', i, 'P')
    x_r[i]=tablevalue('Mix1Array', i, 'x_r')
    rho_l_sat[i]=tablevalue('Mix1Array', i, 'rho_l_sat')


    x_o[i]=1-x_r[i]
    P_sat[i]=Pressure(fluid$, T=T[i], x=0.5)
```

```
        rho_o[i]=993.89 -0.75658*(T[i]-273)        {from Martz thesis, eq 4.1, RL68H}

        v_o[i]=1/rho_o[i]

        v_l_sat[i]=VOLUME(fluid$, T=T[i], x=0)

        v_bar_o[i]=v_o[i]*MW_o                {molar specific volume--for Wilson eqs}

        v_bar_r[i]=v_l_sat[i]*MW              {molar specific volume--for Wilson eqs}



"!============================MODEL PARAMETERS

========================="

{Uncomment the equations for the model being evaluated}

"…………………..WILSON……………..”

A_12[i]=v_bar_o[i]/v_bar_r[i]*exp(-(la2)/(R_u*T[i]))      {Wilson adjustable parameters}

A_21[i]=v_bar_r[i]/v_bar_o[i]*exp(-(la1)/(R_u*T[i]))

gamma_r[i]=1/(x_r[i]+A_12[i]*x_o[i])*exp(x_o[i]*(A_12[i]/(x_r[i]+A_12[i]*x_o[i])-

A_21[i]/(x_o[i]+A_21[i]*x_r[i])))               {ln and exp expressions for convergence}

{ln(gamma_r[i])=-ln(x_r[i]+x_o[i]*A_12[i])+x_o[i]*((A_12[i]/(x_r[i]+x_o[i]*A_12[i]))-

(A_21[i]/(x_r[i]*A_21[i]+x_o[i]))))}

"……………..end  WILSON…………….”
```

```
"…………………NRTL……………."
tau_12[i]=(la2)/(R_u*T[i])
tau_21[i]=(la1)/(R_u*T[i])
{alpha_12=-1}                              {!special case (LEMF model) applies to mixtures whose
excess entropy>0. refg-oil mix can be < or > 0}
A_12[i]=exp(-alpha_12*tau_12[i])   {NRTL adjustable parameters}
A_21[i]=exp(-alpha_21*tau_21[i])
ln(gamma_r[i])=(x_o[i]^2*(tau_21[i]*(A_21[i]/(x_r[i]+x_o[i]*A_21[i]))^2+tau_12[i]*A_12[i]
/(x_r[i]*A_12[i]+x_o[i])^2))
"……………..end NRTL……………."


"……………..UNIQUAC……………."


        x_1 or x_r  = mole fraction of component 1--refrigerant,      x_2 or x_o = mole fraction
of component 2--oil}
(gamma_r[i])=exp(gamma_c_ln[i]+gamma_r_ln[i])
gamma_c_ln[i]=x_r[i]*ln(jtheta_r[i]/x_r[i])+x_o[i]*ln(jtheta_o[i]/x_r[i])+n_c/2*(q_r*x_r[i]*ln
(THETA_1[i]/jtheta_r[i])+q_o*x_o[i]*ln(THETA_2[i]/jtheta_o[i]))
```

```
gamma_r_ln[i]=-q_r*x_r[i]*ln(THETA_1[i]+THETA_2[i]*tau_21[i])-
q_o*x_o[i]*ln(THETA_2[i]+THETA_1[i]*tau_12[i])


jtheta_r[i]=r_1*x_r[i]/(r_1*x_r[i]+r_2*x_o[i])          {for a binary system...denominator
for jtheta and THETA are sums of all system components}
jtheta_o[i]=r_2*x_o[i]/(r_1*x_r[i]+r_2*x_o[i])
THETA_1[i]=q_r*x_r[i]/(q_r*x_r[i]+q_o*x_o[i])
THETA_2[i]=q_o*x_o[i]/(q_r*x_r[i]+q_o*x_o[i])
tau_12[i]=(la2)/(R_u*T[i])
tau_21[i]=(la1)/(R_u*T[i])
"…………………end UNIQUAC……………."



"…………………HEIL……………."
 A_12[i]=v_bar_o[i]/v_bar_r[i]*exp(-(la2)/(R_u*T[i]))    { adjustable parameters}
A_21[i]=v_bar_r[i]/v_bar_o[i]*exp(-(la1)/(R_u*T[i]))
tau_12[i]=(la2)/(R_u*T[i])
tau_21[i]=(la1)/(R_u*T[i])
```

```
(gamma_r[i])=exp(-ln(x_r[i]+x_o[i]*A_21[i])+(x_o[i]*(A_21[i]/(x_r[i]+x_o[i]*A_21[i])-
A_12[i]/(x_r[i]*A_12[i]+x_o[i]))+x_o[i]^2*(tau_21[i]*(A_21[i]/(x_r[i]+x_o[i]*A_21[i]))^2+ta
u_12[i]*A_12[i]/(x_r[i]*A_12[i]+x_o[i])^2)))

"…………………end HEIL……………."


"!=====================END MODEL
PARAMETERS================================"


        {----------Peng-Robinson EOS, 1976------------}

        P[i]=(R*T[i]/(v_v[i]-b))-( a*alpha[i]/(v_v[i]*(v_v[i]+b)+b*(v_v[i]-b)))

        alpha[i]=(1+kappa*(1-sqrt(T[i]/T_c)))^2


        {------- fugacity coefficient equations, simplified for only refg in vapor phase, for PR-
EOS------}

        (PHI_r[i])=exp(z[i]-1-ln(z[i]-b1[i])-
a1[i]/(2*b1[i]*sqrt(2))*ln((z[i]+2.414*b1[i])/(z[i]-0.414*b1[i])))

        z[i]=P[i]*v_v[i]/(R*T[i])

        a1[i]=a*alpha[i]*P[i]/(R*T[i])^2
```

```
b1[i]=b*P[i]/(R*T[i])


{----------PHI evaluated at P_sat with PR-EOS--------------------}

P_sat[i]=(R*T[i]/(v_r_sat[i]-b))-( a*alpha[i]/(v_r_sat[i]*(v_r_sat[i]+b)+b*(v_r_sat[i]-b)))

z_sat[i]=P_sat[i]*v_r_sat[i]/(R*T[i])

a1_sat[i]=a*alpha[i]*P_sat[i]/(R*T[i])^2

b1_sat[i]=b*P_sat[i]/(R*T[i])

{ln(PHI_r_sat[i])=z_sat[i]-1-ln(z_sat[i]-b1_sat[i])-a1_sat[i]/(2*b1_sa[i]t*sqrt(2))*ln((z_sat[i]+2.414*b1_sat[i])/(z_sat[i]-0.414*b1_sat[i]))}

(PHI_r_sat[i])=exp(z_sat[i]-1-ln(z_sat[i]-b1_sat[i])-a1_sat[i]/(2*b1_sat[i]*sqrt(2))*ln((z_sat[i]+2.414*b1_sat[i])/(z_sat[i]-0.414*b1_sat[i])))


{----------------gamma-phi equations------------------}

Pe[i]=exp((v_l_sat[i]*(P[i]-P_sat[i]))/(R*T[i]))      {Poynting effect}

gamma_r[i]=y_r*P[i]*PHI_r[i]/(x_r[i]*P_sat[i]*PHI_r_sat[i]*Pe[i])          {definition of activity coefficent. modified Raoult's law and Lewis-Randall rule to account for non-dealities}
```

```
OBJ[i]=((P[i]-P_exp[i])/(P_exp[i]))^2


    AAD_term[i]=abs((P[i]-P_exp[i])/P_exp[i])

    RMS_term[i]=((P[i]-P_exp[i])^2)/(P_exp[i]^2)

    BIAS_term[i]=((P[i]-P_exp[i])/P_exp[i])


End


OBJ_final=sum(OBJ[i], i=1,N)

AAD=sum(AAD_term[i], i=1, N)*100/N

RMS=sqrt(sum(RMS_term[i], i=1, N))*100/N

BIAS=100/N*sum(BIAS_term[i], i=1, N)
```

Appendix E: Model Sensitivity Tables

Table E.1: Evaluation of NRTL model sensitivity to adjustable parameters for R1234ze(E)/RL68H

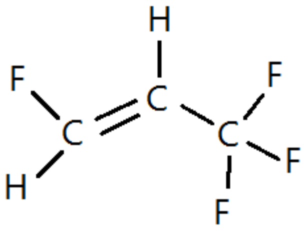
λ_1	λ_2	%AAD	%RMS	%BIAS	%max dev	% max dev x>20
-10000	-10000	54.788	9.458	-54.788	98	88
	-100	54.411	9.383	-54.411	96	88
	0	54.395	9.380	-54.395	96	88
	100	54.378	9.377	-54.378	96	88
	10000	51.199	8.923	-51.199	94	85
-100	-10000	7.916	2.107	-7.807	60	14
	-100	4.783	1.014	-2.734	24	10
	0	4.740	1.009	-2.546	23	10
	100	4.729	1.006	-2.355	22	10
	10000	16.197	3.892	16.077	72	22
0	-10000	7.766	2.077	-7.657	60	14
	-100	4.739	1.009	-2.540	23	10
	0	4.729	1.006	-2.351	22	10
	100	4.721	1.007	-2.158	20	10
	10000	16.5	3.977	16.382	73	22
100	-10000	7.623	2.049	-7.513	59	14
	-100	4.729	1.006	-2.355	22	10
	0	4.722	1.007	-2.164	21	10
	100	4.714	1.010	-1.970	21	10
	10000	16.79	4.058	16.676	74	23
10000	-10000	7.714	1.898	-7.023	55	13
	-100	4.501	0.945	-1.643	21	10
	0	4.530	0.959	-1.445	21	10
	100	4.560	0.976	-1.244	22	10
	10000	18.01	4.398	17.893	77	23
6942.56 (this work)	**-936.00 (this work)**	**4.488**	**0.905**	**-2.311**	**16**	**10**

Table E.2 : Evaluation of Heil model sensitivity to adjustable parameters for R1234ze(E)/RL68H

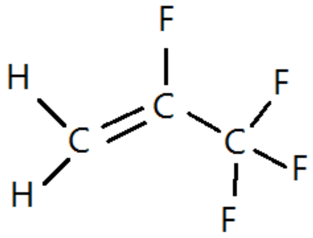
λ_1	λ_2	%AAD	%RMS	%BIAS	%max dev	% max dev x>20
-10000	-10000	57.602	9.878	-57.602	99	98
	-100	57.546	9.868	-57.546	99	98
	0	57.541	9.867	-57.541	99	98
	100	57.537	9.867	-57.537	99	99
	10000	52.467	9.235	-51.275	99	98
-100	-10000	6.955	1.796	-6.774	52	19
	-100	5.957	1.450	-5.463	42	13
	0	5.896	1.428	-5.366	41	13
	100	5.831	1.405	-5.262	40	12
	10000	39.772	11.159	38.787	>100	>100
0	-10000	6.945	1.793	-6.761	52	19
	-100	5.948	1.447	-5.450	42	14
	0	5.887	1.425	-5.352	41	13
	100	5.822	1.402	-5.249	40	12
	10000	39.82	11.18	38.83	>100	>100
100	-10000	6.936	1.790	-6.750	52	19
	-100	5.941	1.444	-5.438	42	13
	0	5.879	1.422	-5.340	41	13
	100	5.814	1.399	-5.237	40	12
	10000	39.855	11.190	38.869	>100	>100
10000	-10000	6.880	1.771	-6.683	51	19
	-100	5.889	1.425	5.364	41	13
	0	5.827	1.403	-5.265	40	12
	100	5.762	1.380	-5.162	40	12
	10000	40.100	11.283	39.108	>100	>100
-5966.60 (this work)	**7737.50 (this work)**	**1.967**	**0.445**	**-0.511**	**14**	**6**

Appendix F: Molecular Descriptions of Components

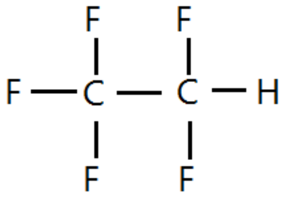
Molecular structures for the refrigerants in the mixtures listed in Table 13 are provided in Figure F.1. Exact molecular structures for the lubricants are not typically known; however, representative molecular descriptions for refrigerant lubricants have been provided in previous studies [33, 61].



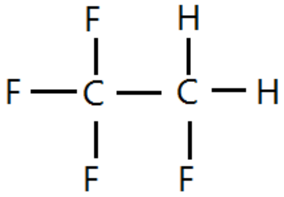
R-1234yf



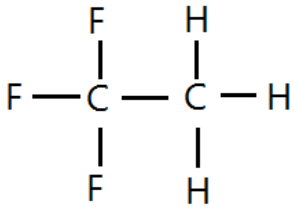
R-1234ze(E)



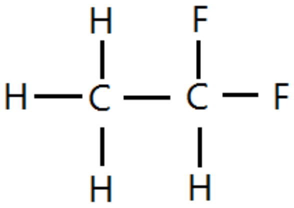
R-125



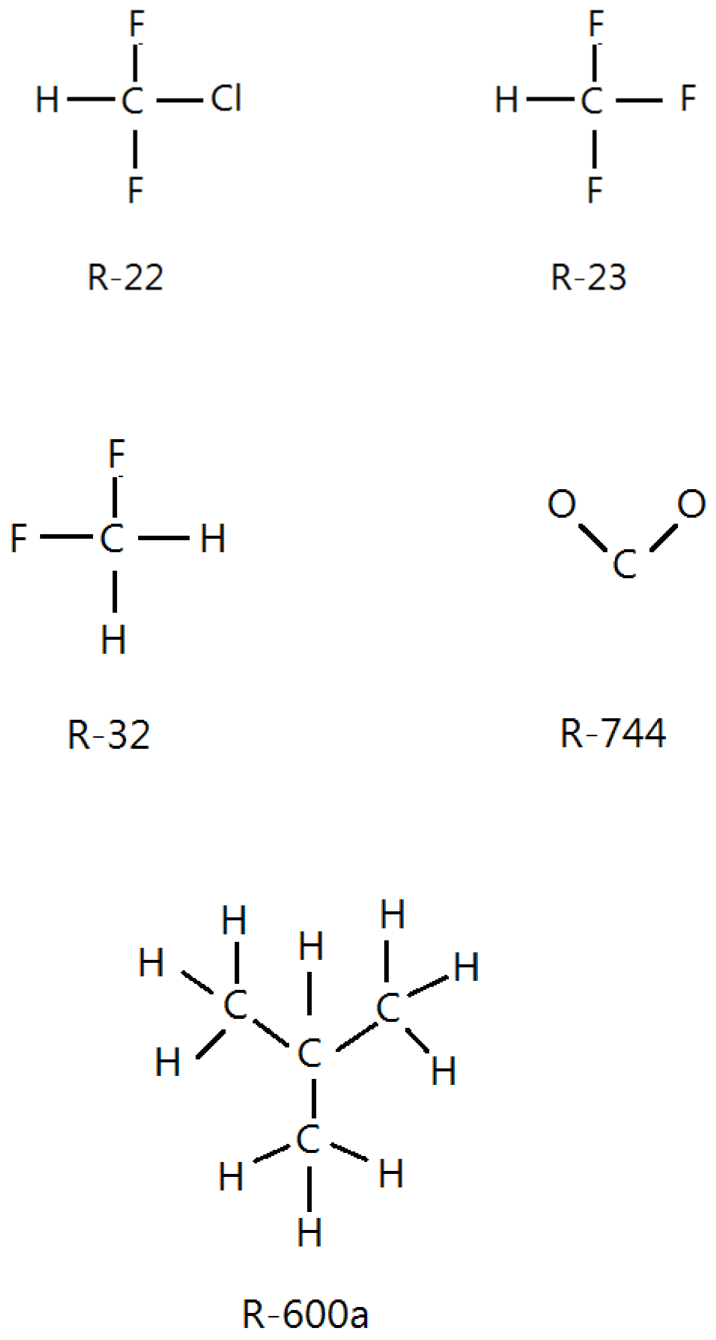
R-134a



R-143a



R-152a



R-22

R-23

R-32

R-744

R-600a

Figure F.1: Molecular diagrams for selected refrigerants