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## Thermophysical property measurements of a novel R-744 blend for heat pump applications

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### ABSTRACT

The phase down of high Global Warming Potential (GWP) refrigerants has encouraged the development of alternative low GWP refrigerants. R-744 has rekindled the interest of suppliers and end users because of its low cost, very low GWP and its non-flammability. These favorable properties notwithstanding, it operates at much higher pressures than fluorocarbon refrigerants and its energy efficiency is penalised by higher ambient temperatures. This study develops a novel refrigerant based on R-744 with added fluorocarbons to reduce pressure and improve efficiency. This blend, “LFR3” comprises R-744 (carbon dioxide); R-32 (difluoromethane) and R-1132a (1,1-difluoroethylene). It is non-flammable and its GWP is less than 150 making it a potentially attractive candidate for use in mobile or stationary heat pump applications or in other applications where R-744 technology has been successfully developed and used. As part of the blend design process a thermodynamic model for the fluid has been developed, including experimental measurement of the blend’s vapor pressure and critical point. Vapor pressure data for the three binary pairs that may be formed from the blend components have been measured from -70 °C to +20 °C. The phase equilibrium data have been regressed using the Peng-Robinson equation of state and Wong-Sandler mixing rules. The paper presents comparison of the experimental and modelled data for the ternary blend and for the binary pairs with each of the phase equilibrium models.

Keywords: LFR3, Vapor pressure, Critical point, low GWP, Thermophysical properties.

### 1. INTRODUCTION

Published data on phase equilibria of systems containing carbon dioxide (R-744) as one of the components are abundant. However, mixtures containing R-744 as the main component of a refrigerant blend are scarce. This particularly holds true for mobile air conditioning and heat pump applications. Heat pump equipment demands environmentally friendly refrigerants whilst simultaneously saving energy and attaining a high coefficient of performance (COP) for attractive utilization. Numerous studies have shown that heat pump water heaters operating with transcritical R-744 can produce hot water with higher temperatures (up to 90°C) whilst adopting higher COP compared with conventional systems (Liu, et al., 2017) (Paniagua, et al., 2019).

Despite the favorable characteristics of R-744 in its pure form, its long expected widespread use has not fully unfolded. The primary reason is due to the technological difficulties. With its higher operating conditions and reduction in energy efficiency, system design changes are often required to overcome these

shortcomings. Additionally, there is limited data of the use of applying blends containing R-744 to existing R-744 technologies.

“LFR3” was developed as a potentially attractive substitute of conventional refrigerants whilst attaining desirable environmental and non-flammability characteristics. LFR3 comprises three components: R-744; R-32; R-1132a in 69; 21; 10% by weight, respectively. Accurate knowledge of thermophysical properties of substitute refrigerants such as “LFR3”, is necessary to evaluate practical performance. Vapor-liquid equilibrium (VLE) data for the three sets of binary mixtures have been measured: R-744 + R-32, R-1132a + R-32, R-744 + R-1132a, in the temperature range of -70 to 20 °C. The R-744 + R-32 data for these isotherms were compared with four literature sets that currently exist: (Adams & Stein, 1971); (Nicola, et al., 2002); (Rivollet, et al., 2004) (Diefenbacher & Turk, 2002). Additionally, the latter three studies investigate the mixture above the critical temperature of R-744 (31 °C). Several studies fit these three sets of vapor liquid equilibrium data to mathematical correlations (Akasaka, 2009) (Mohanty, 2006) (Azari, et al., 2013) (Vaferi, et al., 2018). Whilst these latter studies do not replicate measured data, they provide useful tools for predicting behavior in other systems exhibiting similar conditions.

The saturated pressure and critical property data for the “LFR3” blend have been measured by LTP. This will be presented in this paper and compared with REFPROP V10. No studies yet exist for measuring and correlating data for such R-744 blends.

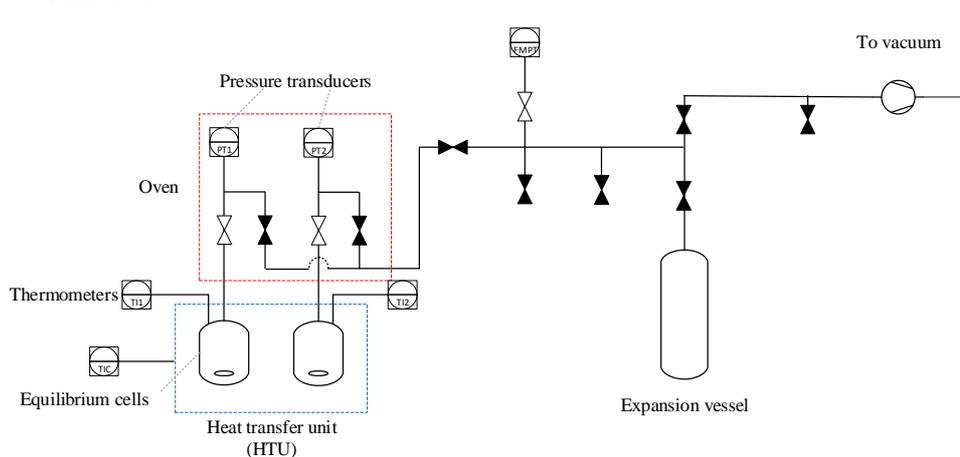
## 2. EXPERIMENTAL

### 2.1 Materials

R-744, R-32 and R-1132a were used with a declared purity of >99.9% and without further chemical purification.

### 2.2 Experimental apparatus

The two main elements of the vapor-liquid equilibrium rig are an equilibrium cell and data collection system as shown in the schematic diagram in **Figure 1**. Rig operation and data collection were automated via system control software. A chiller acts as a thermoregulator controlling the temperature of the heat transfer unit (HTU) surrounding the equilibrium cells (50 cm<sup>3</sup>). For uniform temperature-distribution, two magnetic stirrers with speed controller were fixed below the HTU. To minimize heat transfer losses and ice formation, the HTU was insulated.



**Figure 1:** Static VLE rig

Once stabilized, the HTU temperature fluctuation was controlled to be  $\pm 50$  mK. The temperature in the equilibrium cell was measured by a 100 $\Omega$  platinum resistance thermometer (PRT) (PT100 class 1/10th

DIN) placed in an internal thermowell of the equilibrium cells. The cell PRTs were calibrated using a high precision thermometer with an uncertainty of  $< \pm 1 \text{ mK}$  (used as the standard reference point). The vapor pressure in the cell were measured by electronic pressure transducers with an error of  $\pm 0.04\%$  FS. The pressure transducers were calibrated to a digital primary standard deadweight tester

### 2.3 Experimental procedure

Firstly, the entire static VLE rig was evacuated to  $< 2 \text{ Pa}$ . An intermediate sample cylinder was gravimetrically charged with a predetermined mass of component 1 from the stock material. The desirable mass was translated to pressure using the ideal gas law. The sample cylinder was immersed in liquid nitrogen to drive the material from the stock. To remove non-condensables, the frozen material in the sample cylinder was evacuated before thawing. The three-step process was repeated until the component was non-condensable free ( $< 2 \text{ Pa}$ ). The sample cylinder was weighed using a four-figure balance with a resolution of  $\pm 0.5 \text{ mg}$ .

The equilibrium cells were cooled, followed by charging material from the sample cylinder before reweighing this to determine the mass of component 1 transferred. The cell thermometers, circulator, magnetic plates, and insulation were fitted before starting the temperature profile. Once thermal equilibrium had been reached, the temperature stability within the cells was typically  $< \pm 30 \text{ mK}$  across the isotherms. The profiles were set to  $\geq 120$  minutes at each isotherm. Based on the highest stability of temperature inside the equilibrium cells, 20 minutes of stable vapor pressure data was drawn.

The same method was carried out for charging the second component. The mass charged was determined based on the mole fraction to be studied. The equilibrium cell containing component 1 was frozen and checked for non-condensable material before charging component 2. After the data were measured and run complete, the mixture was gravimetrically charged for the next composition.

### 2.4 Data Reduction Methods

The phase behavior of refrigerants and their mixtures can be represented in terms of thermodynamic fundamentals. Most vapor-liquid mixtures adopt non-ideal behaviors simultaneously when vapor and liquid phases of each species are mixed. Deviations from ideal state manifest themselves in many ways; these are typically presented in terms of activity coefficient models (ACM) or equations of state (EoS) - based on the same thermodynamic principles. In addition, empirical correlations allow the user to manipulate an unlimited matrix of parameters until optimal fit is achieved to experimental data.

Many commonly used methods for parameter estimation provide no measures of uncertainty. This is usually achieved by calculation of dependent variables at each experimental point, summation of the squared differences between calculated and measured values, and adjustment of parameters to minimise the overall difference. These methods do not consider for errors in the measured independent variables. Literature investigating vapor-liquid equilibrium, errors in independent variables such as measured liquid-phase mole fraction, temperature are often underestimated. The total pressure is a function of the estimated parameters, measured temperature, and liquid phase mole fraction.

Vapor-liquid equilibrium equipment with integrated compositional measuring techniques have been utilized by various scientists (Yang, et al., 2013) (Adams & Stein, 1971) (Nicola, et al., 2002). Authors such as Akasaka (2009) fit these data in later years to the molar volumes to  $\pm 2\%$  and an AAD of 0.82% but do not fit the PVT data on an all-inclusive basis to improve the accuracy. The scarcity of the data for the low critical point mixtures comprising this blend indicates complexity of the experimental set-up to accurately withdraw at equilibrium, measurement repeatability whilst simultaneously leaving the composition of the mixture in the cell undisturbed.

### 3. MODEL

#### 3.1 Model selection utilized

Wilson-Redlich-Kwong (Wilson-RK) and Peng-Robinson Wong Sandler (PRWS) were the two primary selections, providing the lowest relative deviation from experimental data. The Wilson expressions are provided in Orbey and Sandler (1998). The PR EoS is given by the following expression:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \quad (1)$$

This cubic EoS was combined with the Mathias-Copeman alpha ( $\alpha$ ) function and WS mixing rules involving the non-random two liquid (NRTL) model, to account for the intermolecular attraction forces. The expressions are provided in Rivollet *et al.* (2004).

#### 3.2 Optimization

To optimise these models, the adjustable parameters were obtained by minimizing the objective function, resulting in best model performance. The objective function can take different forms. For this work, it is represented by the following:

$$F = \frac{100}{N} \left[ \sum_{i=1}^N \left( \frac{|P_{exp} - P_{calc}|}{P_{exp}} \right)^2 \right] \quad (2)$$

Where N is the number of experimental data and  $P_{exp}$  and  $P_{calc}$  are the measured and calculated pressures respectively. To improve the fit further, initial interaction parameters were provided after the first simulation to provide a starting point for the sets of data following this.

## 4. RESULTS & CORRELATIONS

#### 4.1 Vapor pressures of pure components

The measured saturated vapor pressures of pure R-744, R-1132a and R-32 for each binary mixture comprising LFR3 were compared with the calculated data from REFRPOP V10, and the results are listed in Table 3. The critical properties for are provided in Table 2.

**Table 2:** Critical properties of pure components comprising LFR3

Compound	T <sub>c</sub> (K)	P <sub>c</sub> (MPa)
R-744	304.1	7.38
R-1132a	302.8	4.46
R-32	351.3	5.78

The average absolute deviation (AAD) and absolute average relative deviations (AARD) are expressed as absolute and relative differences between the experimental and REFRPOP V10 predicted saturated vapor pressures for the pure components comprising LFR3:

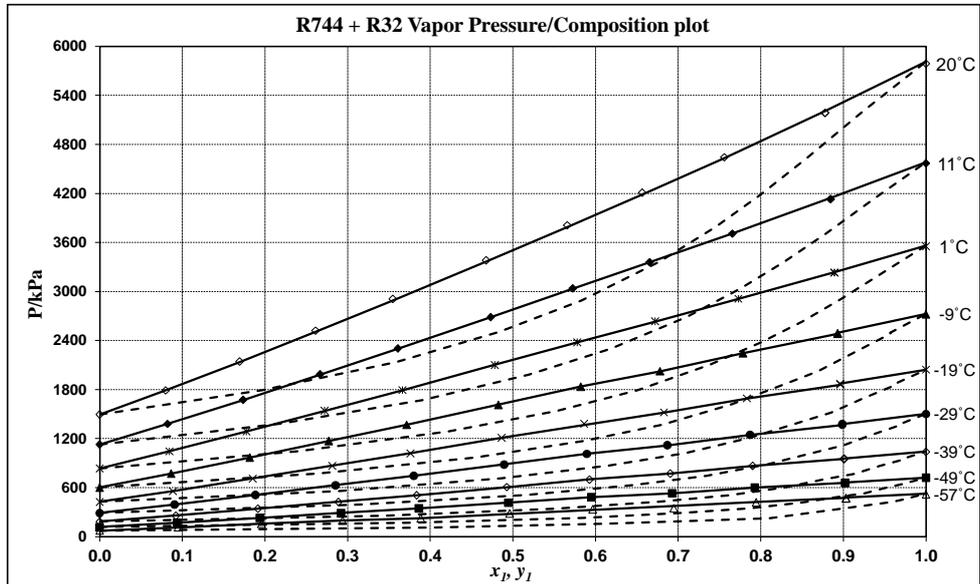
**Table 3:** Saturated vapor pressures of pure components comprising LFR3

Compound	T range (K)	Pressure AAD (kPa)	Pressure AARD (%)
R-744	222.15-293.15	0.0011	0.08
R-1132a	201.15-283.15	0.0038	0.04
R-32	213.15-293.15	0.0018	0.11

Good agreement is observed between the experimental and REFRPOP V10 predicted vapor pressures of the pure components. These results validated the quality of the mixture data. The experimental and correlated data of VLE for binary systems; R-744 + R-32, R-1132a + R-32, R-744 + R-1132a, and their respective AADs are presented.

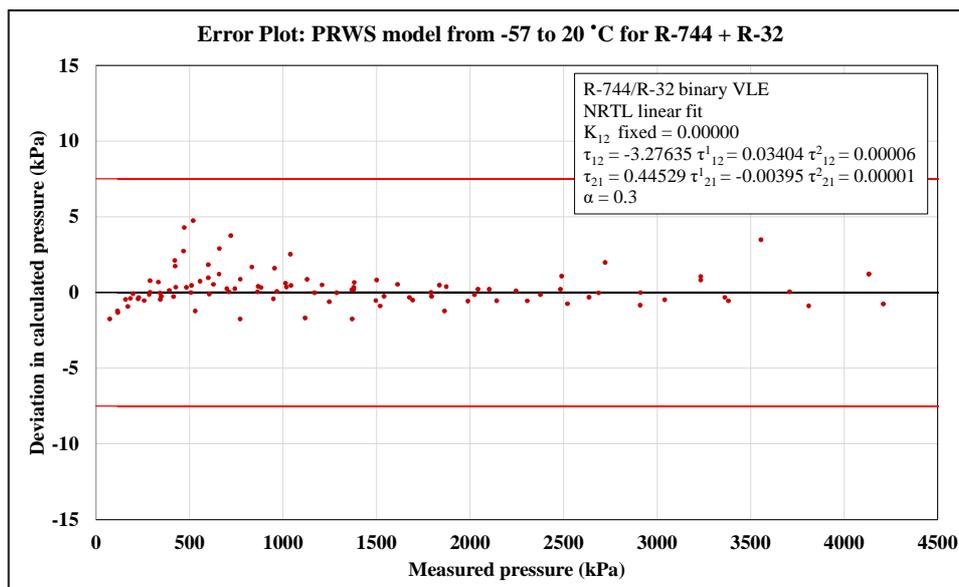
#### 4.2 Vapor liquid equilibrium of R-744 + R-32

Figure 2 contains a summary plot of the vapor liquid equilibrium measured (data points) and calculated (solid lines) from -57 to 20°C:



**Figure 2:** Vapor pressure measurements of R-744 + R-32 vs mole fraction of R-744

From **Figure 2** it is shown that R-744 is completely soluble in R-32 across all isotherms studied in this range. The VLE exhibits zeotropic behavior and can be considered as ideal in terms of Raoult's law. Qualitative and consistent agreement is observed to the results at similar temperatures of studies by Adams & Stein (1971); Nicola *et al.* (2002); Rivollet *et al.* (2004) and Diefenbacher & Turk (2002). The comparison of measured and calculated pressures for the R-744 + R-32 system for 9 isotherms between 213.15-293.15 K are shown below. The AAD and AARD between measured and model predictions are 2.64 Pa and 0.26% respectively.



**Figure 3:** PRWS model of R-744 + R-32 – deviation between measured & calculated pressure

### 4.3 Vapor liquid equilibrium of R-744 + R-1132a

Figure 4 contains the VLE measured between -58 to 10 °C:

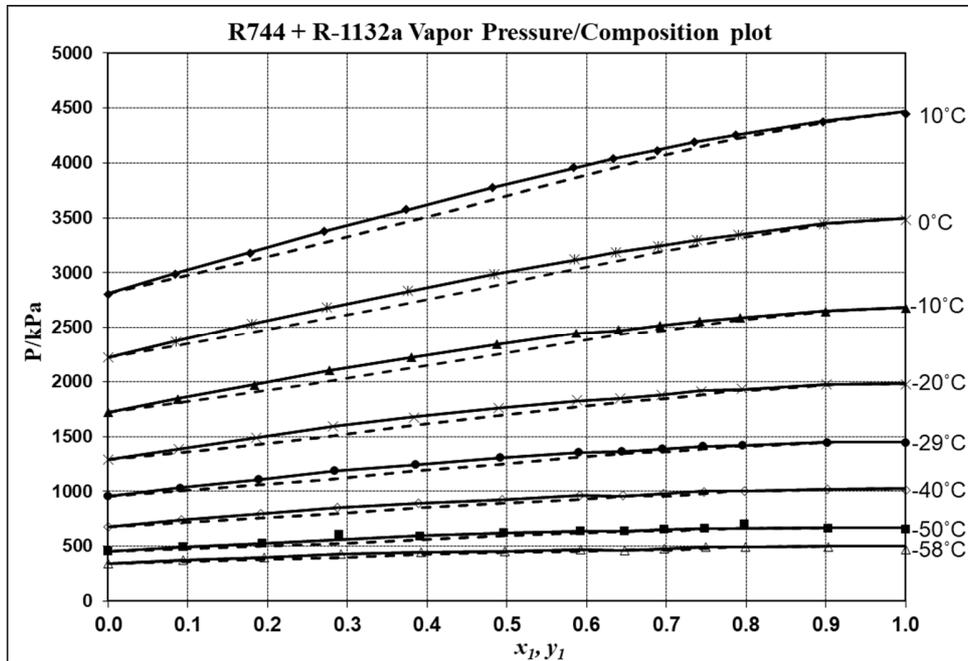


Figure 4: Vapor pressure measurements of R-744 + R-1132a vs mole fraction of R-744

Similarly, R-744 + R-1132a is soluble in the mixture across the 201.15-283.15 K isotherms studied. Unlike R-744 + R-32, it exhibits slightly positive deviation from Raoult's law and subtle non-ideal behavior. Figure 5 expresses the differences between experimental & calculated pressures using NRTL and PRWS. The AAD and AARD are 2.72 Pa and 0.28% respectively.

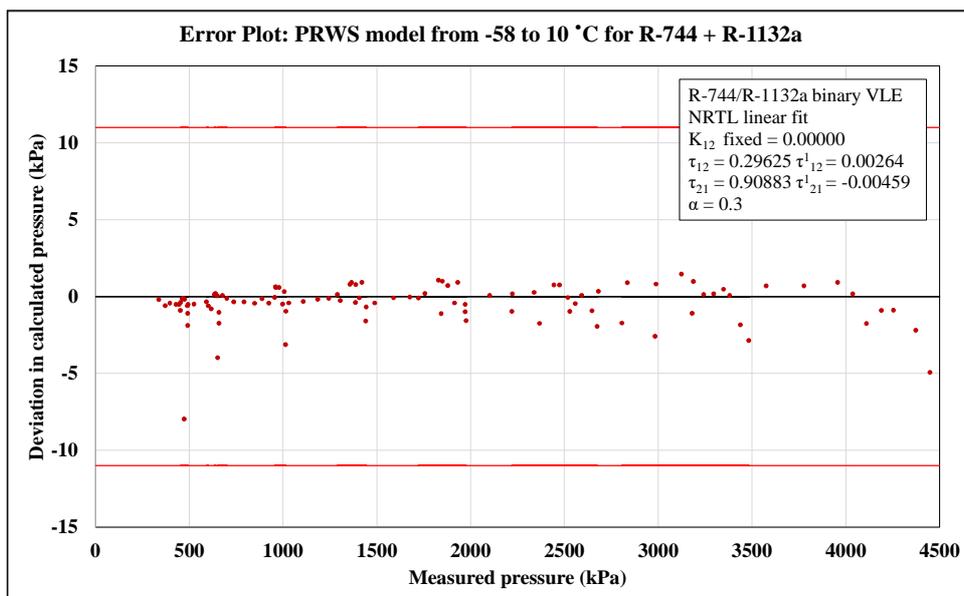


Figure 5: PRWS model of R-744 + R-1132a – deviation between measured & calculated pressures

#### 4.4 Vapor liquid equilibrium of R-1132a + R-32

Figure 6 contains the VLE measured between -73 to 11 °C:

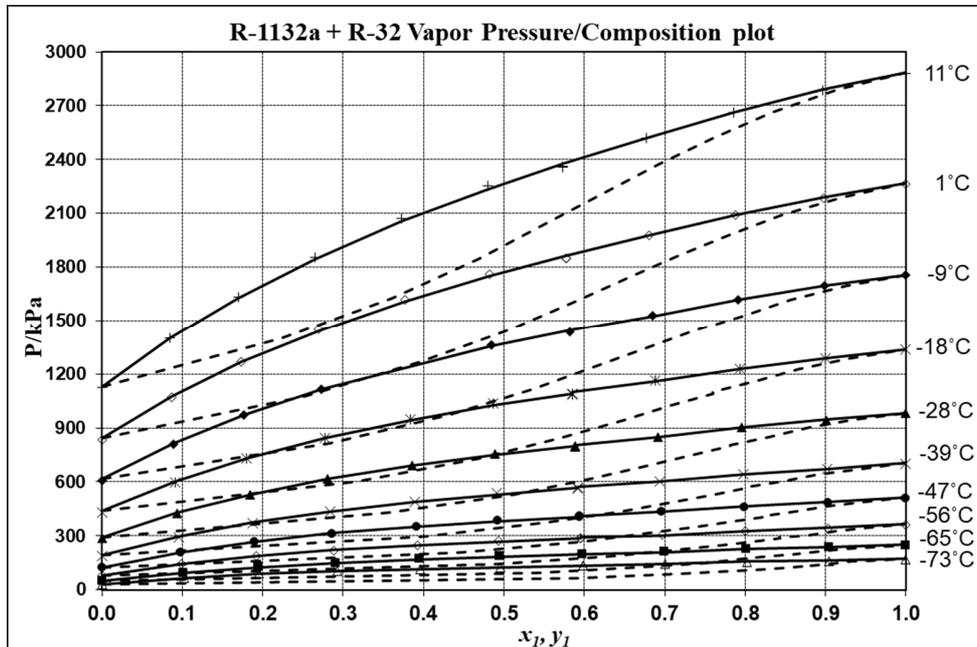


Figure 6: Vapor pressure measurements of R-1132a + R-32 vs mole fraction of R-1132a

Figure 7 shows differences between experimental & calculated pressures:

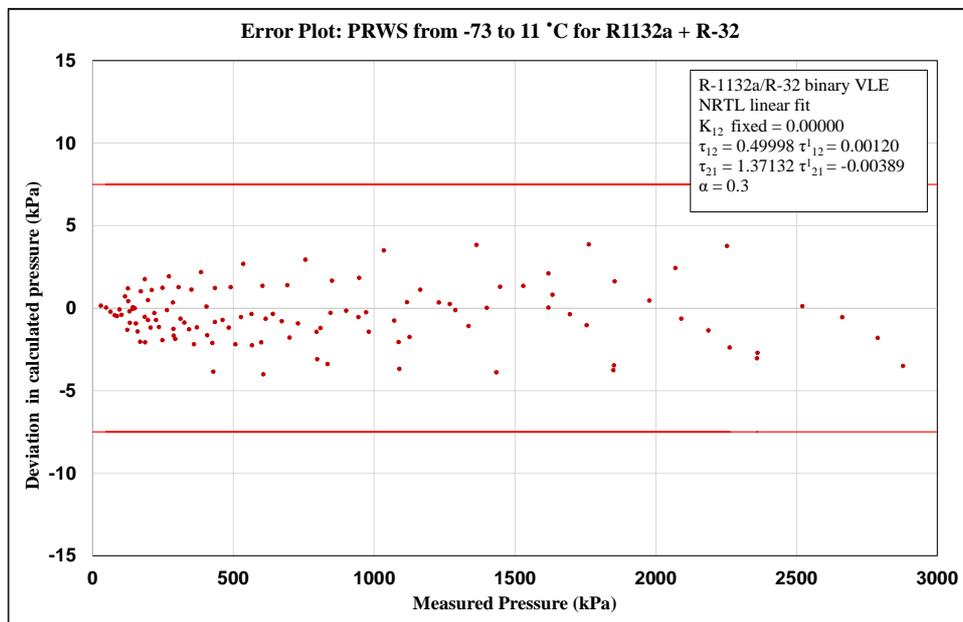


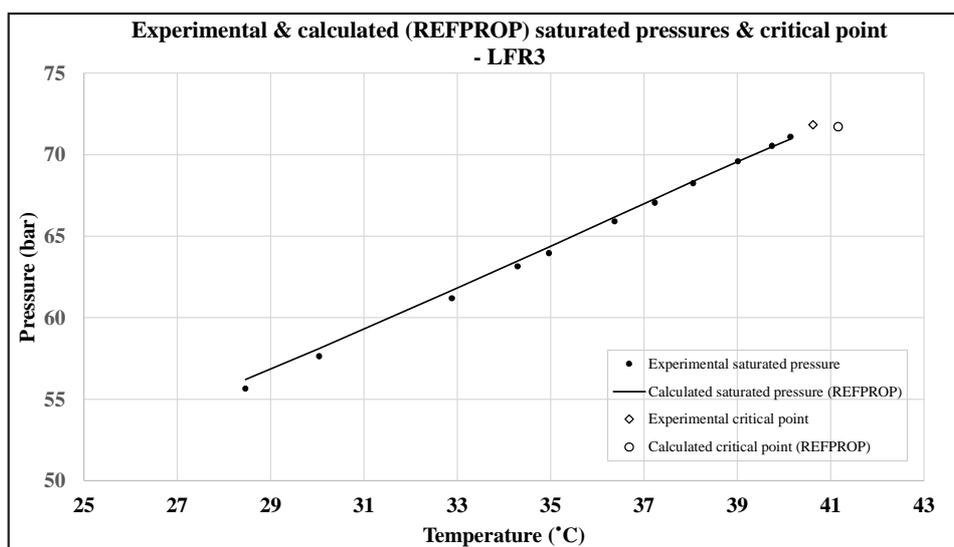
Figure 7: PRWS model of R-1132a + R-32 – deviation between measured & calculated pressures

The AAD and AARD are 6.35 Pa and 0.64% respectively. R-1132a + R-32 has a stronger positive deviation from Raoult's law compared to R-744 + R-1132a. R-1132a is a hydrofluoroolefin (HFO) and due to its molecular structure, its presence in the mixture evidently results in weaker intermolecular attractions in its

mixtures – particularly with R-32, than when used in its pure form. Dissimilarly, R-744 + R-32 have stronger attractions in the intermolecular bonds resulting in its ideal behavior observed in **Figure 2**. This is likely due to the interaction of hydrogens in hydrofluorocarbons (HFCs) with R-744 (Nicola, et al., 2002).

#### 4.5 LFR3 experimental critical point & saturation pressure

The results of the critical point and saturation pressure measurements for LFR3 are shown in **Figure 8**. The experimental measurements are compared to REFPROP V10.



**Figure 8:** Experimental and calculated (REFPROP V10) saturated pressures, critical point of LFR3\*

Overall, there is very good agreement between the experimental and REFPROP V10 estimated saturated pressures for LFR3.

\*Measurements provided by LTP

## 5. CONCLUSION

We measured the data for three binary mixtures; R-744 + R-32; R-744 + R-32 and R-1132a + R-32 in the temperature range of -70 to 20°C. The data was successfully fitted to PRWS with an AARD <  $\pm 0.7\%$  between measured and calculated data. As an improvement to R-744, LFR3 produces all the benefits of using R-744 as a working fluid. All the data was measured within the expected accuracy of the  $\pm 5$  kPa, temperature of  $\pm 0.1$  K, and 0.1% on the composition.

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