

EXPERIMENTAL CHARACTERIZATION OF PHASE EQUILIBRIUM, LIQUID DENSITY AND VISCOSITY OF A MIXTURE OF R-744 (CO₂) AND POLYOL ESTER OIL

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Abstract. *In recent years, the interest in R-744 (CO₂) as refrigerant in light commercial systems has seen an increase due to its zero Ozone Depletion Potential (ODP) and low Global Warming Potential (GWP). In the present paper, solubility, density and viscosity of a mixture of R-744 and a synthetic polyol ester (POE) ISO 68 oil are presented for temperatures between 12 and 75°C. A specially constructed experimental facility that enables simultaneous measurements of the physical properties is described in the manuscript. The experimental results indicate the occurrence of miscibility gaps at moderate mass fractions and temperatures lower than the critical temperature of the pure refrigerant. Evidence of Liquid-Liquid Equilibrium is also inferred from the behaviour of experimental density as a function of pressure. Empirical correlations for saturation pressure as a function of solubility and temperature and for the liquid viscosity are proposed.*

Keywords: *Oil-refrigerant mixtures, natural refrigerants, Phase equilibrium, R-744, polyol ester oil.*

1. INTRODUCTION

There are several refrigeration applications where R-744 (CO₂) is well suited as a primary refrigerant (Pettersen, 1999). It is the only non-flammable, non-toxic natural refrigerant that is capable of operating in a vapour compression cycle at temperatures lower than 0°C. However, despite the increasing number of publications dealing with mixtures of R-744 and lubricant oils in recent years, much development is still needed before the most suitable lubricants that operate reliably with this refrigerant are finally selected. In this respect, data on phase equilibrium and physical properties are of utmost importance due to their impact on the system operating parameters (such as equalizing pressure) and on compressor performance and reliability.

With some exceptions, the majority of reports in the open literature do not cover extensive temperature and/or concentration ranges and conclusions regarding phase equilibria and physical properties behaviour of a particular mixture (as well as the performance of a given modelling approach) become limited to the ranges of the independent variables employed in each study. Seeton *et al.* (2000) investigated experimentally the solubility and viscosity of mixtures of R-744 and four ISO 220 synthetic lubricant oils (PAO, AB, PAG and POE). The tests were undertaken at an oil concentration of 90% (weight) to represent typical compressor conditions. The temperature was varied between -20 and 120°C for each mixture. The authors concluded that the PAG, AB and PAO were not miscible in R-744 at high refrigerant concentrations (typically higher than 50% in weight). However, they observed good lubrication characteristics in the R-744/PAO mixture for transcritical applications due to the higher viscosities exhibited by this mixture under those conditions. Hauk and Weidner (2000) investigated experimentally the phase behaviour and viscosity of mixtures of R-744 and three synthetic oils (POE, PAG and PAO) at temperatures ranging from 5 to 100°C and pressures up to 150 bar. They identified regions of Vapour-Liquid-Liquid Equilibrium (VLLE) in all mixtures. R-744 was found to be more soluble in the POE oil (which resulted in lower viscosities for the R-744/POE mixture). Barotropic behaviour (i.e., an oil-rich liquid phase less dense than the refrigerant-rich liquid phase) was seen in the R-744/PAO mixture under certain conditions. Youbi-Idrissi *et al.* (2003) carried out an experimental study to determine the solubility of R-744 in a PAG ISO 120 oil between -20 and 60°C. A region of immiscibility was observed at refrigerant mass fractions higher than 50%. An empirical correlation was proposed to calculate the solubility as a function of pressure and temperature. Tsuji *et al.* (2004) presented an experimental facility to measure the solubility and density of mixtures of R-744 and lubricant oils. The apparatus was firstly validated with measurements of phase equilibrium and density of R-744/n-decane. Measurements were carried out with a mixture of R-744 and a PAG ISO 56 at 71°C. The authors used the Peng and Robinson (1976) equation of state to correlate their solubility and density data. The agreement was satisfactory for the bubble-point pressure predictions, but significant deviations were observed in

the density calculations. Tsuji *et al.* (2005) measured simultaneously the solubility, liquid density and viscosity of mixtures of R-744/POE ISO 70 and R-744/PAG ISO 56 at 104°C and pressures up to 20.11 MPa. n-Decane and TEG were employed as model substances. The authors observed an increase in R-744 solubility with pressure for PAG and POE and, for TEG, regions of VLLE were observed. Two trends were observed in the density behaviour as a function of saturation pressure. A convex shape was seen for R-744/POE and a concave shape for R-744/TEG and R-744/PAG. According to the authors, the latter was an indication of Liquid-Liquid Equilibrium. Bobbo *et al.* (2005) measured the solubility of R-744 in five pentaerythritol esters and in commercial ester oil (Castrol Icematic SW32) at 10°C. Mixed deviations with respect to Raoult's law were observed in all mixtures with some indication of immiscibility at molar fractions higher than 94% in one of the mixtures. In a subsequent study, Bobbo *et al.* (2006) reported measurements of solubility of R-744 at 60°C in three commercial POE lubricant oils (Castrol Icematic SW32, ICI Emkarate RL32S and Mobil EAL Artic 32). A chromatographic analysis revealed significant differences in composition between the lubricant oils. However, differences between R-744 solubility in each lubricant were negligible. Seeton and Hrnjak (2006) determined experimentally the density, viscosity and surface tension of a R-744/POE ISO 32 mixture for refrigerant mass fractions (solubility) up to 85% and temperatures between -30°C and 125°C. The authors observed a region of immiscibility between -20 and 30°C for mass fractions above 40%. Empirical correlations and a Daniel chart were proposed for solubility, density and viscosity.

The objective of this paper is to present experimental data on phase equilibrium (saturation pressure and solubility), density and viscosity of a mixture of R-744 and POE ISO 68 oil. The data were obtained at temperatures between 12 and 75°C. Departure from ideal behaviour was quantified in terms of refrigerant activity and excess molar volume. Empirical correlations for the saturation pressure and mixture viscosity are proposed.

2. EXPERIMENTS

2.1. Experimental Apparatus and Procedure

The experimental facility is schematically illustrated in Figure 1. Initially, a specified amount of lubricant oil is placed in the equilibrium cell (2). The cell is an AISI 316L stainless steel cylinder with an inside diameter of 102 mm (15 mm wall thickness) and an internal volume of approximately 4 L. A vacuum pump (Edwards EIM18) generates a vacuum of 0.04 mbar in the apparatus to remove moisture and dissolved gases. An initial amount of refrigerant is fed into the system through the valve located on the top end of the test cell. The system temperature is set by a thermostatic bath (1) (MQTB, Microquimica) that circulates service water through a tank (6) in which the equilibrium cell is fully immersed. In the present experiments, the pressure of the oil-refrigerant mixture is, therefore, a dependent variable. The equilibrium cell is instrumented for absolute pressure, P , (HBM P3MB, 20 MPa), and temperature of the fluids in the cell is recorded by three type-T thermocouples (T_1 , T_2 , T_3) (Omega, TMQSS) located at three distinct heights to measure the temperatures of the liquid and vapour phases. A gear pump (Micropump GC-M25JF5S6) (5) moves the liquid oil-refrigerant mixture through the experimental facility. The speed of the electrical motor is set at its minimum value (12 Hz). The mixture first flows through a Coriolis-type mass flow transducer (Danfoss, DI 1.5) (4) that records flow rate, temperature and liquid density. Then, an oscillating piston viscometer (Cambridge Applied Systems, SPL 571) (3) registers temperature and dynamic viscosity of the liquid mixture. The solubility of the mixture is measured gravimetrically using a liquid mixture sample collected in a 150 mL cylinder (7). The experimental apparatus is integrated with a signal conditioning module (National Instruments, BNC2120) (8) and a computerized system for data acquisition and treatment (9).

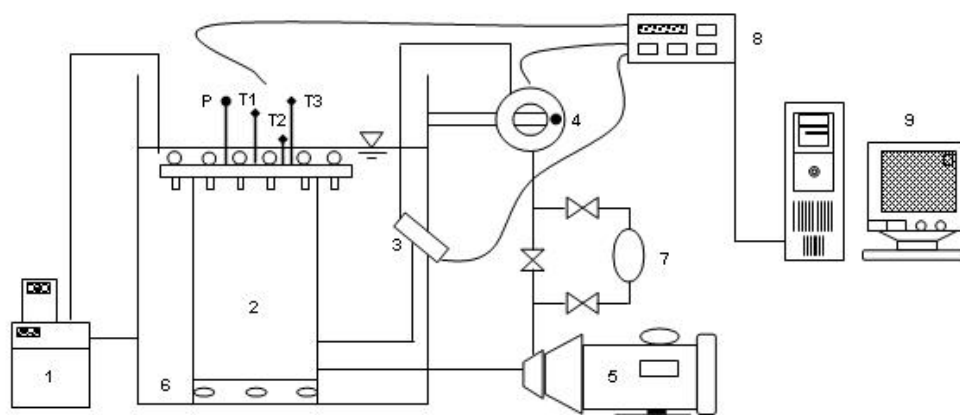


Figure 1. Schematic representation of the experimental rig.

After thermodynamic equilibrium is reached (which may take from 3 to 5 hours and is characterized by the equality of temperatures in the equilibrium cell and by constant readings of pressure and density), data are recorded and averaged over a 5 minute interval (1000 data samples per channel), and a liquid sample is collected for solubility measurement. The sample is placed on a precision balance (KNWaagen, KN400) and the total amount of oil and liquid refrigerant is recorded. Vacuum (0.04 mbar) is applied to the cylinder to vaporize the refrigerant. Care is taken so that oil droplets are not carried along by the refrigerant vapour, and an oil separator is mounted on the cylinder's outlet for this purpose. After evacuation is complete, the mass of oil is recorded. The mass of the evacuated cylinder plus the oil separator is known *a priori* and is subtracted from the total mass given by the balance before and after evacuation. The solubility is given by,

$$x_R = \frac{m_R}{m_R + m_O} \quad (1)$$

where m_O and m_R are the masses of oil and refrigerant in the liquid sample. m_R is calculated by subtracting the mass of oil from the total mass of the sample.

The procedure is repeated for another value of solubility (and hence bubble-point pressure) at a constant temperature by adding a controlled amount of refrigerant into the system. Tests were also carried out starting from pure refrigerant (or from a mixture with a low oil concentration) in the equilibrium cell and decreasing the solubility on the same isotherm by adding evacuated oil samples through the 150 mL cylinder. Under some conditions, very different (but consistently observed) *PVT* results were obtained with the two different procedures. It is believed that these are linked with the occurrence of a phase separation in the liquid, as will be discussed later.

The thermocouples were calibrated to $\pm 0.2^\circ\text{C}$ and the uncertainty of the density measurements was $\pm 1\%$ of the absolute reading (declared by the manufacturer). The uncertainty of the viscosity measurement (also declared by the manufacturer) was $\pm 1\%$ of the full scale (FS) (0.1cP for the 0.1-10 cP piston, 1 cP for the 1-100 cP piston). The uncertainty of the pressure transducer was $\pm 1\%$ FS (0.2 MPa) and that of the balance was ± 0.03 g. After an error propagation analysis (Marcelino Neto, 2006), it was concluded that the uncertainty in the determination of solubility was ± 0.5 g/kg. This value was subsequently confirmed through repeatability tests.

The experimental procedure was validated with vapour pressure and density measurements of pure R-744 and with density of an ISO 10 lubricant oil. The reference data for vapour pressure of R-744 were calculated from REFPROP 7.0 (Lemmon *et al.*, 2002) and the lubricant oil reference data were available from the ISO 10 oil manufacturer. The mean absolute deviations for vapour pressure and density of R-744 between 5 and 30°C were less than 1% and 3%, respectively. The mean absolute deviation of the ISO 10 oil density was 3% for temperatures between 10 and 50°C .

2.2. Experimental Conditions

The experimental conditions of the experiments reported here were as follows. Solubility and liquid density of R-744/POE ISO 68 were measured simultaneously for temperatures ranging from 12 to 75°C . In these runs, the oscillating piston viscometer was not mounted on the experimental rig because the system pressure attained during the experiments (~ 12 MPa) surpassed the maximum working pressure stated by the manufacturer (7.45 MPa). Subsequent experimental runs were carried out to measure simultaneously the mixture viscosity together with solubility and density at temperatures and pressures ranging from 36 to 76°C and 900 to 5800 kPa, respectively (typical conditions of R-744 compressors). R-744 was supplied by AGA (99.9% pure) and the lubricants were supplied by Embraco. The molecular mass of the lubricant oil lies between 600 and 900 kg/kmol and its exact molecular composition is proprietary information.

3. RESULTS

3.1. Solubility and Phase Equilibrium

The experimental data (68 points in total) for equilibrium pressure as a function of R-744 equilibrium liquid mass fraction (solubility) and temperature (12, 25, 35, 55 and 75°C) are shown in Figure 2 for the R-744/POE ISO 68 mixture. For 12 and 25°C , i.e., temperatures lower than the critical temperature of R-744 (30.98°C), the equilibrium curves at a given temperature were obtained using two different procedures. In the first approach, the experiment was initiated with pure refrigerant in the experimental rig (or with just a small amount of oil in it) and, as small oil mass increments were added to the system, the decrease in equilibrium pressure was observed and recorded. In the second approach, there was initially pure oil (in vacuum) in the rig and, as pure refrigerant was gradually added to the system, the increase in equilibrium pressure was recorded.

At 12°C , there were no differences between the equilibrium curves obtained following the two different procedures described above. Similar phase equilibrium behaviour was observed by Bobbo *et al.* (2005) for a R-744/POE ISO 32 mixture at 0°C . However, as can be seen from Figure 2, a very distinct trend was seen at 25°C according to each

procedure (closed and open symbols). Starting with pure refrigerant, the equilibrium pressure remained equal to the saturation pressure of R-744 at 25°C (~6.45 MPa) up to equilibrium mass fractions near 60%. From this point on, the equilibrium pressure decreased with the addition of oil to the system (open symbols). Following the inverse procedure, i.e., adding pure refrigerant into a mixture initially with a high oil concentration, an abrupt inflexion in the solubility curve is observed at equilibrium mass fractions around 60% (closed symbols).

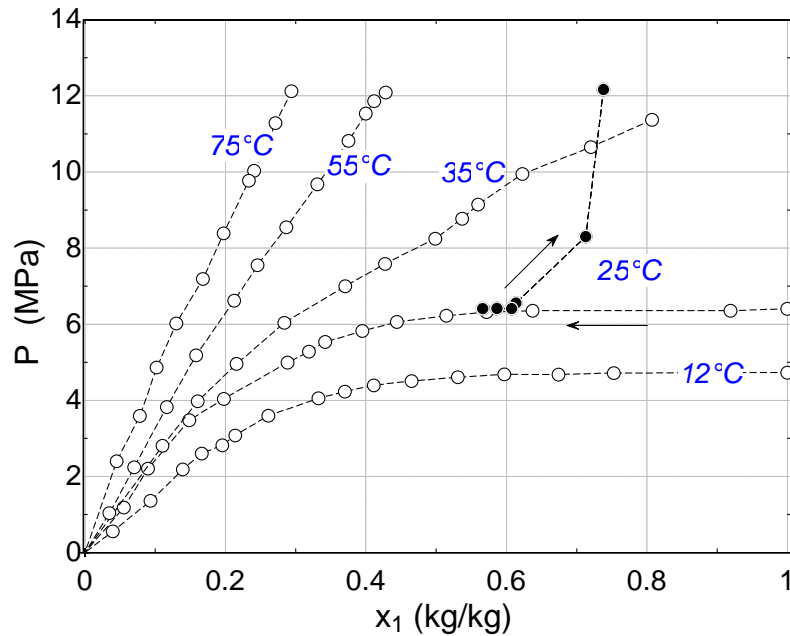


Figure 2. Phase equilibrium of R-744/POE ISO 68.

Although the experimental apparatus does not enable a direct visual observation of the oil-refrigerant mixture, it is believed that this behaviour is an indication of immiscibility and phase separation in the liquid. Similar observations were reported by Hauk and Weidner (2000) for a R-744/POE mixture at 25°C. Their experimental facility allowed visual access to the oil-refrigerant mixture and two liquid phases were identified. Analogously to what has been observed by Hauk and Weidner at 25°C, it can be concluded that for equilibrium refrigerant mass fractions higher than that associated with the point of inflection, there are three phases in thermodynamic equilibrium: two liquid phases (one with a higher refrigerant concentration and another with a low refrigerant concentration) and one vapour phase. At 35, 55 and 75°C, the solubility increases with pressure. This is also in line with what was observed by Hauk and Weidner (2000) and by Bobbo *et al.* (2006) for R-744/POE ISO 32 mixture at 60°C.

3.2. Departure from ideality

The vapour phase departure from ideal gas behaviour was quantified through the fugacity coefficient given by (Peng and Robinson, 1976),

$$\ln \hat{\phi}_i^V = \ln \left(\frac{\hat{f}_i}{\bar{y}_i P} \right) = \frac{b_i}{b} (Z - 1) - \ln(Z - b) - \frac{a(T)}{2\sqrt{2}b} \left(\frac{2 \sum_{j=1}^n \bar{y}_j a_{ij}}{a(T)} - \frac{b_i}{b} \right) \ln \left(\frac{Z + 2.414b}{Z - 0.414b} \right) \quad (2)$$

where a , b , a_{ij} and b_j are parameters in the Peng and Robinson (1976) equation of state (PR EoS), and Z is the compressibility factor obtained solving the cubic PR EoS given P , T and \bar{y}_i (the molar fraction of component j in the vapour). The vapour phase fugacity coefficient as a function of molar solubility is shown in Figure 3. As expected, the departure from ideal gas behaviour increases with temperature and with refrigerant concentration due to increase in pressure associated with it.

The departure from ideality in the liquid phase was analyzed in terms of the refrigerant activity given by,

$$a_R = \frac{\hat{\phi}_R^V P}{\hat{\phi}_R^{sat} P_R^{sat} P_e} \quad (3)$$

This is shown as a function of temperature in Figure 4 for the R-744/POE ISO 68 mixture. As can be seen, the mixture exhibits large mixed deviations with respect to Raoult's law (solid line). Negative deviations (predominance of attraction molecular forces) exist at refrigerant molar fractions lower than approximately 90% and positive deviations are seen above 90%. This is in quantitative agreement with the behaviour identified by Bobbo *et al.* (2005) for R-744/POE mixtures. In addition, Figure 4 indicates that for this particular mixture, non-ideality is more influenced by concentration than by temperature.

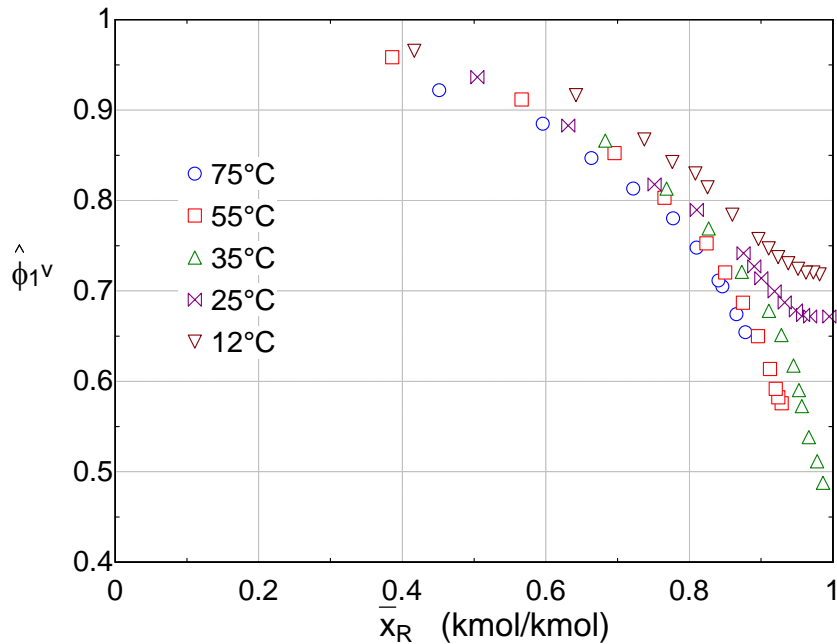


Figure 3. Vapour phase fugacity coefficient of R-744 as a function of equilibrium liquid molar fraction and temperature (R-744/POE ISO 68).

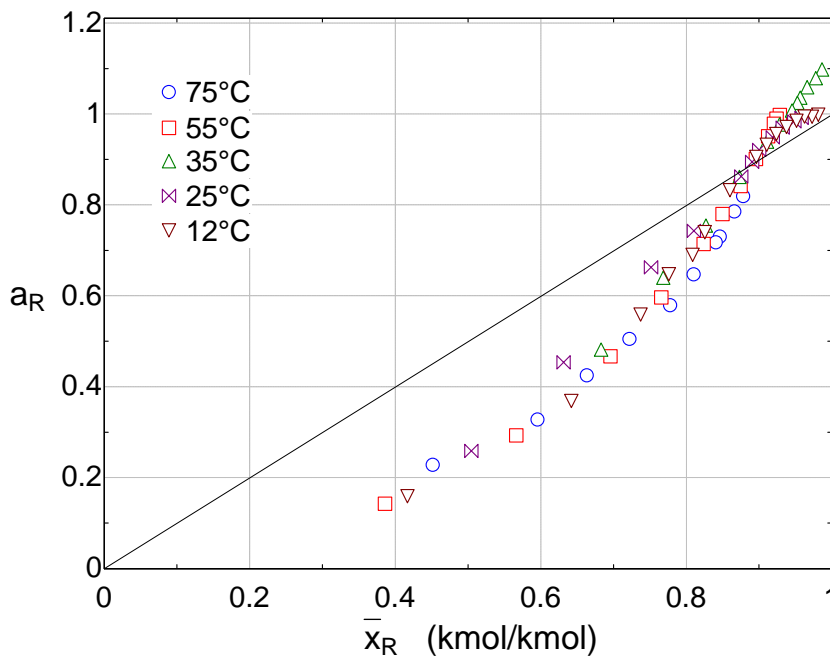


Figure 4. Refrigerant activity in the R-744/POE ISO 68 mixture.

In order to calculate the refrigerant activity reported in Figure 4, several hypotheses were made in Equation (3). First, the Poynting factor, Pe , was assumed equal to unity. Also, an extrapolation of Antoine's equation was utilized to estimate the saturation temperature of the refrigerant,

$$\log_{10} P_R^{sat} = A - \frac{B}{T + C - 273.15} \quad (4)$$

where the saturation pressure and temperature are in kPa and K, respectively. A , B and C are empirical coefficients given by 7.52161, 1384.861 and 74.840 (Poling et al., 2000). Although saturation pressures calculated for temperatures above 30.98°C (the critical temperature of R-744) have no physical meaning, the extrapolation allowed an assessment of the departure from ideality for all data points. Grebner *et al.* (1993) utilized an identical procedure to evaluate the deviations from ideal solution behaviour in R-134a/POE mixtures. In fact, extrapolations such as these give reasonably accurate results for low molar fractions of the solute (in this case, R-744) and temperatures near the critical temperature of the solute (Assael *et al.*, 1996; Elliot and Lira, 1999).

Alternatively, the concept of standard state fugacity (already implicit Equation 3) defined as,

$$f_R^0 = \phi_R^{sat} P_R^{sat} \exp\left[\frac{V_R^L (P - P_R^{sat})}{RT}\right] \quad (5)$$

could have been defined in terms of Henry's law for $\bar{x}_R \rightarrow 0$, i.e., $f_R^0 = He$. In this case, Henry's constant, He , can be estimated directly from the experimental data. In the present work, this approach was not pursued because the large differences between the molecular weights of the oil and the refrigerant makes the acquisition of phase equilibrium data for $\bar{x}_R \rightarrow 0$ prone to large experimental uncertainties.

3.3. Correlation Development

An empirical correlation for the equilibrium pressure as a function of temperature and solubility was devised for the R-744/POE ISO 68 mixture. Based on the expression utilized by Jeng *et al.* (2001), the following relationship is put forward,

$$P = \zeta_1 x_1 + \zeta_2 x_1 T + \zeta_3 x_1^2 + \zeta_4 x_1^2 T + \zeta_5 x_1^2 T^2 \quad (6)$$

where T is in K and P in MPa. The empirical coefficients ζ_i were adjusted using the experimental data for each oil-refrigerant mixture through an optimization (genetic) algorithm (Klein, 2004) to find a minimum of the objective function,

$$Ob = \sum_{i=1}^n (P_{cal,i} - P_{exp,i})^2 \quad (7)$$

The search interval for each empirical coefficient was from -1000 to 1000 and the optimum values of the coefficients are summarized in Table 1. The correlation is limited to temperatures between 12 and 75°C and should not be used with other types of oil and refrigerant solubilities higher than 0.4 with POE ISO 68. Figure 5 illustrate the performance of the correlation in comparison with the experimental data. The root mean square (RMS) deviation, average absolute deviation (AAD) and the Bias defined through Eqs. (8)-(10) are 1.64, 8.68 and -1.756%, respectively.

$$RMS = \frac{100}{n} \sqrt{\sum_{i=1}^n \frac{(P_{cal,i} - P_{exp,i})^2}{P_{exp,i}^2}} \quad (8)$$

$$AAD = \frac{100}{n} \sum_{i=1}^n \left| \frac{P_{cal,i} - P_{exp,i}}{P_{exp,i}} \right| \quad (9)$$

$$Bias = \frac{100}{n} \sum_{i=1}^n \frac{P_{cal,i} - P_{exp,i}}{P_{exp,i}} \quad (10)$$

Table 1. Empirical coefficients in the phase equilibrium correlation.

| ζ_1 | ζ_2 | ζ_3 | ζ_4 | ζ_5 |
|-----------|-----------|-----------|-----------|------------|
| -93.15 | 0.3863 | -97.12 | 0.5151 | -0.0008038 |

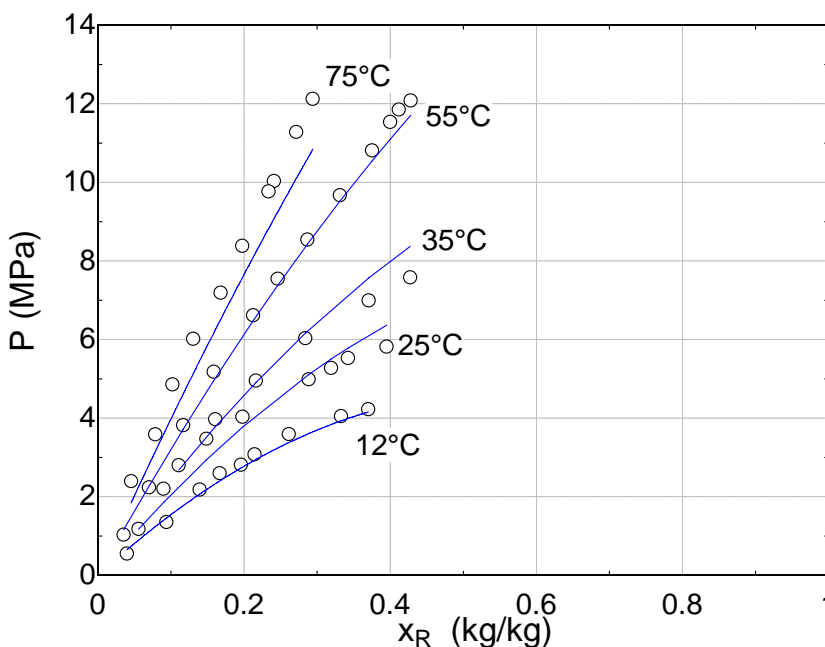


Figure 5. Correlation for predicting phase equilibrium in the R-744/POE ISO 68 mixture.

3.4. Density and Excess Molar Volume

Experimental density as a function of refrigerant molar fraction and temperature is shown in Figure 6. The corresponding ideal mixture density calculated from Equations (11) and (12) is shown for comparison.

$$V^{id} = \bar{x}_R V_R + (1 - \bar{x}_R) V_O \tag{11}$$

$$\frac{1}{\rho^{id}} = \frac{V^{id}}{\bar{x}_R M_R + (1 - \bar{x}_R) M_O} \tag{12}$$

In Equation (11), the pure refrigerant molar volume was also calculated at the saturation pressure given by the extrapolation of Antoine's equation (Poling et al., 2000). Figure 6 reveals the existence of large positive deviations from ideal behaviour, indicating a predominance of molecular attraction forces (Elliot and Lira, 1999). Experimental densities obtained at the conditions in which liquid phase separation took place are also shown in Figure 6 (closed symbols).

The behaviour of density as a function of saturation pressure at 25°C and 55°C is shown in Figures 7.a-b. At 25°C, as the system pressure approaches the pure refrigerant saturation pressure (~ 6.45 MPa), the mixture density decreases toward an asymptotic value. This behaviour was interpreted by Tsuji *et al.* (2005) as a progressive reduction of the mixture's ability to absorb more refrigerant with increasing pressure. The change of slope in the density-pressure curve characterizes the appearance of a second liquid phase. This phase has a higher refrigerant concentration and its density increases with saturation pressure. A change of slope and the appearance of a second liquid phase were not observed at 55°C at pressures lower than 12 MPa. Therefore, according to Tsuji *et al.*'s interpretation, the mixture at this temperature still exhibits certain availability for absorbing refrigerant. This does not mean, however, that an inflexion point (and hence a second liquid phase) cannot appear at higher pressures.

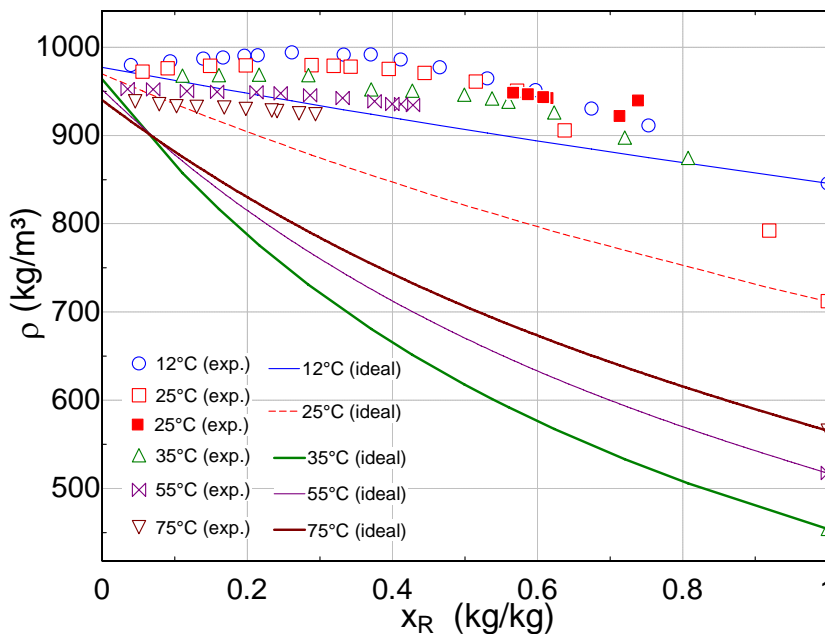


Figure 6. Experimental density and ideal solution density model for R-744/POE ISO 68.

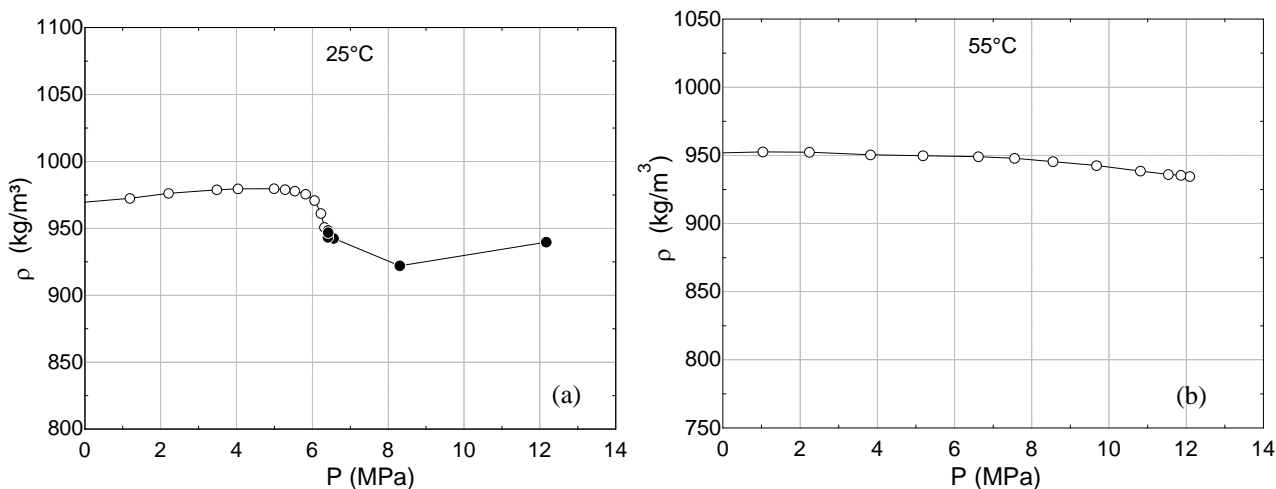


Figure 7. Behaviour of liquid density as a function of saturation pressure.
 (a) Isotherm with phase separation, (b) Isotherm without phase separation.

The experimental excess molar volume calculated from Equation (13) is shown in Figure 8 as a function of mixture temperature. A peak in excess volume was observed between molar fraction of 0.8 and 1, with a similar trend for all temperatures. The deviations from ideal solution behaviour increase with temperature up to 35°C and, at higher temperatures the magnitude of the deviations decrease with increasing temperature. This is due to the value of the pure refrigerant molar volume calculated extrapolating Antoine’s equation that decreases with increasing temperature.

$$V^E = \frac{\bar{x}_R M_R + (1 - \bar{x}_R) M_O}{\rho} - V^{id} \tag{13}$$

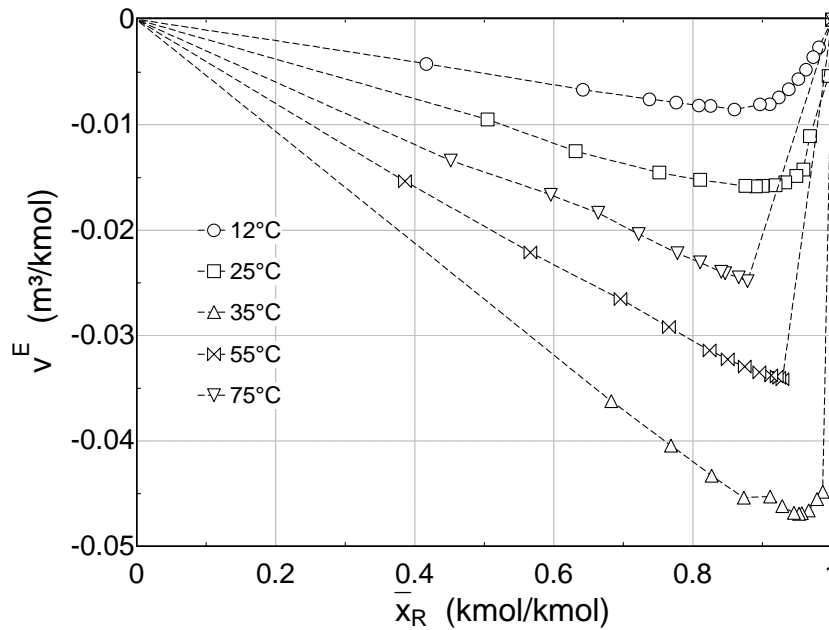


Figure 9. Experimental excess molar volume for R-744/POE ISO 68.

3.5. Viscosity and Activation Energy for Viscous Flow

As with the other physical properties, the liquid mixture viscosity exhibits large deviations with respect to the ideal solution viscosity (Figure 10). The ideal mixture viscosity is calculated from (Poling *et al.*, 2000)

$$\ln \eta = \bar{x}_R \ln \eta_R + (1 - \bar{x}_R) \ln \eta_O \quad (14)$$

In Equation (14), the pure refrigerant viscosity was estimated at the saturation pressure given by the extrapolation of Antoine's equation (Poling *et al.*, 2000). Because the temperatures of the mixture viscosity experimental runs were above the critical temperature of the pure refrigerant (30.98°C), the pure refrigerant viscosity increases with increasing temperature (i.e., as in a gas). As the pure oil viscosity decreases with increasing temperature, a crossing is observed at a molar solubility between 0.8 and 0.9.

A first attempt to predict the mixture viscosity was carried out using a modified version of the correlation of Grunberg and Nissan (1949). The modified correlation uses a two-term Redlich-Kister expansion (Smith *et al.*, 2000) for the activation energy for viscous flow as follows

$$\ln \eta = \bar{x}_R \ln \eta_R + (1 - \bar{x}_R) \ln \eta_O + \left[\psi_1 (1 - \bar{x}_R) \bar{x}_R + \psi_2 (1 - \bar{x}_R)^2 (\bar{x}_R)^2 \right] RT \quad (15)$$

The empirical coefficients ψ_i were obtained through an optimization (genetic) algorithm (Klein, 2004) to find a minimum of the objective function,

$$Ob = \sum_{i=1}^n (\eta_{cal,i} - \eta_{exp,i})^2 \quad (16)$$

The search interval for each empirical coefficient was from -100 to 100 and the optimum values of the coefficients were $\psi_1 = 7.977$ and $\psi_2 = 9.847$. The RMS deviation, AAD and Bias associated with the correlation are 12.27, 31.26 and -9.91%, respectively.

As can be seen from the above values and from Figure 10, the performance of the correlation is not so satisfactory. Although the agreement with the experimental data is good at low refrigerant molar solubilities (around 0.4), the correlation does not perform well at low oil molar fractions. More research (experimental and theoretical) is needed to find a more suitable approach to predict the liquid mixture viscosity in the present system.

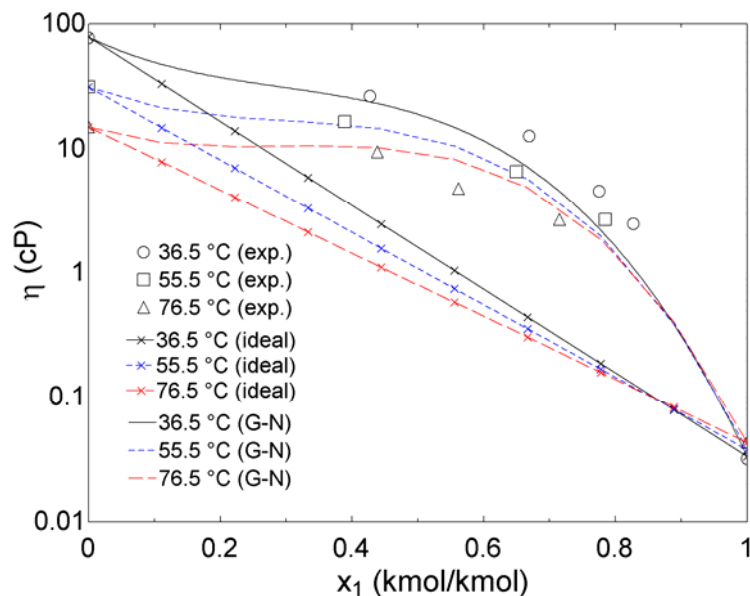


Figure 10. Predictions of absolute viscosity for R-744/POE ISO 68.

4. Conclusions

The present paper put forward new data on phase equilibrium (saturation pressure and solubility), liquid density and viscosity of a mixture of R-744 (CO₂) and POE ISO 68 lubricant oil. An experimental facility that enables simultaneous measurements of the physical properties was utilized. The data were obtained for two distinct sets of experimental runs. In the first set, temperatures were varied between 12 and 75°C for values of refrigerant solubility ranging from near 0 to 1. In this set, because of the high saturation pressures attained by the system, the mixture viscosity was not measured. In the second set of experiments, solubility, density and viscosity were measured simultaneously at temperatures and pressures ranging from 36 to 76°C and 900 to 5800 kPa, respectively.

The phase equilibrium data related to the first set of experiments showed that regions of immiscibility exist at temperatures lower than the critical temperature of the refrigerant at moderate mass fractions (30-60%). Significant departure from ideal behaviour, quantified through the refrigerant activity and excess molar volume, was observed.

In the second set of experiments, the viscosity exhibited large deviations with respect to the ideal solution behaviour. Some improvement in the viscosity prediction was obtained with an extended Grunberg and Nissan (1949) correlation. However, more data are needed and further correlation types need to be tested before a more satisfactory prediction approach can be delivered.

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REFERENCES

- Assael, M.J., Trusler, J.P.M. and Tsolakis, T.F., 1998, "Thermophysical Properties of Fluids: An Introduction to their Prediction", Imperial College Press, London, 353p.
- Bobbo, S., Scattolini, M., Camporese, R., Fedele, L. and Stryjek, R., 2005, "Solubility of carbon dioxide in pentaerythritol esters", Proc. of IIR 2005 Vicenza Conference – Thermophysical Properties and Transfer Processes of Refrigerants, Vicenza, Italy, 193-200.
- Bobbo, S., Scattolini, M., Camporese, R., Fedele, L. and Stryjek, R., 2006, "Solubility of carbon dioxide in some commercial POE oils", Proc. of 7th IIR Gustav Lorentz Conference on Natural Working Fluids, Norway, 409-411.
- Elliot, J.R. and Lira, C.T., 1999, "Introductory Chemical Engineering Thermodynamics". Prentice Hall, 660p.
- Grebner, J.J. and Crawford, R.R., 1993, "Measurement of pressure-temperature-concentration relations for mixtures of R-12/mineral oil and R-134a synthetic oil", ASHRAE Transactions, Vol. 99, part 1.
- Hauk, A. and Weidner, E., 2000, "Thermodynamics and fluid-dynamic properties of carbon dioxide with different lubricants in cooling circuits for automobile application", Ind. Eng. Chem. Res., 39, 4646-4651.
- Klein, S.A., 2004, *Engineering Equation Solver*, Professional Version.

- Lemmon, E.W., McLinden, M.O. and Huber, M.L., 2002, REFPROP v.7.0, NIST Standard Reference Database 23, NIST, USA.
- Marcelino Neto, M.A., 2006, "Characterization of Thermophysical Properties of Mixtures of Lubricant Oil and Natural Refrigerants", M.Eng. Dissertation (in Portuguese), Federal University of Santa Catarina, 168 p.
- Peng, D.Y. and Robinson, D.B., 1976, "A new two-constant equation of state", *Ind. Eng. Chem.* 15(1), 59-64.
- Pettersen, J., 1999, "Carbon dioxide (CO₂) as a primary refrigerant", Proceedings of the Centenary Conference of the Institute of Refrigeration, ImechE, November 10-11, London, UK.
- Poling, B.E., Prausnitz, J.M. and O'Connell, J.P., 2000, "The Properties of Gases and Liquids". McGraw-Hill, New York, 5th Ed.
- Seeton, C.J., Fahl, J. and Henderson, D., 2000, "Solubility, viscosity, boundary lubrication and miscibility of CO₂ in synthetic lubricants", Proc. 4th IIR-Gustav Lorentzen Conference of Natural Working Fluids at Purdue, pp. 417-24.
- Seeton, C.J. and Hrnjak, P., 2006, "Thermophysical properties of CO₂-lubricant mixtures and their affect on 2-phase flow in small channels (less than 1 mm)", Proc. Int. Refrigeration and Air Conditioning Conference at Purdue, Paper R170, July 17-20.
- Smith, J.M., Van Ness, H.C., Abbott, M.M., 2000, "Introdução à Termodinâmica da Engenharia Química", 5^a Ed., LTC Editora, Rio de Janeiro.
- Tsuji, T., Tanaka, S., Hiaki, T. and Saito, R., 2004, "Measurements of bubble point pressure for CO₂ + decane and CO₂ + lubricating oil", *Fluid Phase Equilibria* 219 pp. 87-92.
- Tsuji, T., Namikawam D., Hiaki, T., Saito, R. and Ito, M., 2005, "Simultaneous measurement of solubility, density and viscosity of lubricants with CO₂ (R-744) at high temperature and pressures for refrigerating systems", Proc. IIR 2005 Vicenza Conference – Thermophysical Properties and Transfer Processes of Refrigerants, Vicenza, Italy, pp. 185-91.
- Youbi-Idrissi, M., Bonjour, J., Terrier, M.F., Meunier, F. and Marvillet, C., 2005, "Solubility of CO₂ in a synthetic oil". Proc. International Congress of Refrigeration 2003, Washington, D.C., Paper R0300.