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PHASE EQUILIBRIUM DATA FOR R-290 + POE ISO 32 MIXTURES BETWEEN 283.15 AND 343.15 K

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Abstract. *The selection of the most suitable working fluids for refrigeration and ORC (Organic Rankine Cycle) applications is based on a number of criteria, including lubricating oil solubility/miscibility. The lubricating oil used in expanders comes into contact with the working fluid and may migrate from the expander to other parts of the system, giving rise to some problems, such as oil accumulation in the heat exchangers. Therefore, a deeper knowledge of the thermodynamic behavior of R-290/lubricant systems is essential for a proper oil selection used in expanders of ORC systems. To that end, the aim of the present work is to investigate experimentally the phase behavior of R-290/POE ISO 32 binary mixtures. Experimental bubble point pressures for R-290/POE ISO 32 have been measured over a temperature range from 283 to 343 K with R-290 mole fractions ranging from 0.2 to 0.8. A total of 20 experimental points is reported with combined expanded uncertainties (k = 2) ranging from 1.5% to 18.1%.*

Keywords: *Organic Rankine Cycle, Phase equilibrium, Mixture, Hydrocarbons, Lubricating oil*

1. INTRODUCTION

Propane (R-290) and other natural fluids have been considered as promising drop-in replacements to conventional refrigerants due to their low Global Warming Potential (GWP). The lubricating oil used in expanders comes into contact with the working fluid and may migrate from the expander to other parts of the system, giving rise to problems such as oil accumulation in the heat exchangers. Therefore, a deeper knowledge of the thermodynamic behavior of R-290 + lubricant oil systems is essential for a proper oil selection used in expanders of ORC systems.

In the literature, there is significantly less studies on phase behavior of R-290 + lubricant mixtures compared to other hydrocarbons, such as isobutane (R-600) and synthetic refrigerants. Czubinski *et al.* (2020) measured bubble point pressures for the system R-290 + POE ISO 22 and correlated with Peng and Robinson (1976) and *PC-SAFT* (Gross and Sadowski, 2001) equations of state. More recently, Wang *et al.* (2021) investigated experimentally the solubility of R-290 in two mineral lubricants and correlated the data with the NRTL (non-random two-liquid) activity coefficients model.

The aim of the present work is to investigate experimentally the phase behavior of R-290 + POE ISO 32 binary mixtures using a variable inner volume synthetic apparatus. To validate the apparatus and the experimental procedure, measurements with CO_2 + R-1234yf binary system were conducted over the full temperature range and compared with published vapor-liquid equilibrium data. Comparisons with equations of state will be presented in the full paper.

2. EXPERIMENTS

2.1 Apparatus description

A schematic of the experimental apparatus is shown in Figure 1. Details concerning the instrumentation are given elsewhere (Marcelino Neto *et al.*, 2014a e Czubinski *et al.*, 2019), so only a brief description will be provided here. The main component of the apparatus is the equilibrium cell, which consists of a cylindrical vessel of 17.3 mm internal diameter, 50 mm external diameter, with its inner volume divided by a movable piston into two chambers. The front chamber houses the fluid system being tested and is equipped with two sapphire windows which allow visual observation of all the space inside the cell. At the top of the front chamber, two ports fitted with reducing unions are used as fluid inlet-outlet and pressure-temperature taps, respectively. At the bottom of the cell, a port is used as the R-290 inlet.

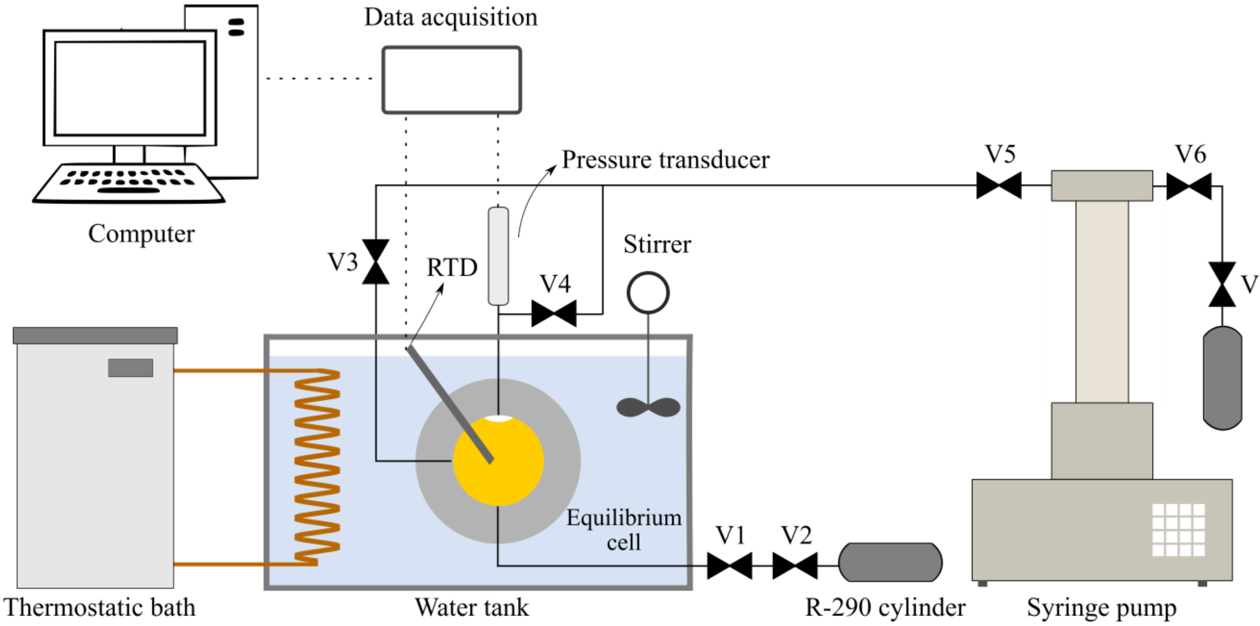

Figure 1. Schematic of the apparatus used to make bubble point measurements.

2.2 Method of measurement

For the synthetic method, the mixture is prepared in the equilibrium cell with a precisely known composition and the properties are measured in the equilibrium state. An extensive review about synthetic and other methods for vapor-liquid equilibrium (VLE) measurement is presented in Dohrn *et al.* (2012).

Prior to use, the system was thoroughly leak tested over the whole operating pressure range with nitrogen, cleaned several times with an adequate solvent (R-141b), flushed with nitrogen and subjected to vacuum pressures for some hours in order to eliminate possible traces of solvent. The fluid R-290 is charged first into the front chamber through valves V1 and V2. The amount of R-290 charged into the system is determined by weighing a reservoir before and after the charge using a precision balance (Shimadzu model 620H). After that, lubricating oil POE ISO 32 was introduced into the syringe pumps through valves V6 and V7 respectively. To insert the POE ISO 32 in the cell, the chamber of the syringe pump and the equilibrium cell were set at approximately 20 °C. The total mass of lubricant inserted in the front chamber was given by its density and the volumetric displacement provided by the syringe pump. Finally, the rear chamber is pressurized to push the piston toward the front chamber until the vapor phase disappears in the front chamber (visual observation via the sapphire window). The system is mechanically agitated with a magnetic stirrer to reach the equilibrium state, which is determined from the stability of pressure and temperature measurements.

The bubble point pressure is obtained by expanding the front chamber and decreasing the mixture pressure in small steps until the appearance of a second phase, while simultaneously recording temperature and pressure of the front chamber. The appearance of the second phase is identified by visual inspection with the aid of a digital camera, and by an abrupt change in slope in the real-time pressure measurements when the bubble point pressure is reached. To check the repeatability of the results, measurements were repeated three times at each temperature.

2.3 Experimental materials

The experimental materials used in the present work are specified in Table 1. The table lists the refrigerants, CAS number, and manufacturer's stated purity. Prior the measurements, the lubricating oil POE ISO 32 was degassed by using an ultrasonic liquid processor (Sonics, model VCX 500) for at least 10 minutes. All other fluids were used without further purification.

Table 1. Fluid sample technical data and purity.

Material	Source	CAS number	Purity
Carbon dioxide	Linde	124-38-9	99.999%
R-1234yf	Honeywell	29118-24-9	99.9%
Propane	Air Liquide	74-98-6	99.99%
POE ISO 32	Emkarate	-	-

2.4 Experimental uncertainty analysis and validation

The expanded uncertainty for the bubble-point pressure measurements is calculated by the root sum of squares of three principles sources of uncertainty: *(i)* temperature, *(ii)* pressure, and *(iii)* mixture composition. The standard combined uncertainty of the temperature measurements is determined from the uncertainties in the RTD calibration. The expanded uncertainty (k = 2) of calibration procedure is estimated to be 0.17 K. The pressure transducer was calibrated *in-situ* for pressures ranging from 1 to 50 bar with a piston gauge (DH-Budenberg model 580-series). It is estimated that the expanded uncertainty of the pressure transducer after calibration was 0.1 bar (0.2 % of the full-scale reading) with a coverage factor k = 2. The uncertainty of the sample composition was estimated combining the uncertainties of the precision balance, lubricating oil density, syringe pump displacement and dead volume in the tubing between V1 and V2.

The phase equilibrium experimental procedure was validated by measuring the VLE of pure R-290 and the binary system (R-1234yf + CO_2). The bubble point pressures were compared with the available literature data (Juntarachat *et al.*, 2014; Arami-Niya *et al.*, 2020). The results for bubble-point pressure for pure propane and R-1234yf + CO_2 mixtures are presented in Tables 2 and 3, respectively. The absolute deviations $|p - p_{ref}|$ were less than 0.016 MPa, which is within the expanded uncertainty (k = 2) of the experimental measurements.

Table 2. Measured bubble point pressures, p, for propane at temperature T.

T [K]	p [MPa]	U (p) [MPa]	p_{ref} $^{(a)}$ [MPa]	p-p_{ref} [MPa]	100 × (p-p_{ref})/p_{ref}
283.59	0.648	0.021	0.644	0.004	0.62
306.93	1.189	0.022	1.183	0.007	0.57
321.02	1.634	0.022	1.635	-0.002	-0.10
340.61	2.469	0.023	2.461	0.009	0.36
348.58	2.879	0.024	2.873	0.007	0.23

(a) Values calculated from a reference equation of state available in REFPROP 9.1 (Lemmon *et al.*, 2013).

Table 3. Measured bubble point pressures, p, for the system CO_2 (1) + R-1234yf (2) at temperature T and liquid mole fraction x_1 .

x_1 [-]	T [K]	p [MPa]	U (p) [MPa]	p_{ref} [MPa]	p-p_{ref} [MPa]	100 × (p-p_{ref})/p_{ref}
0.1274	292.97	1.078	0.022	1.080$^{(a)}$	-0.02	-0.20
0.1676	338.23	3.016	0.034	3.032$^{(b)}$	-0.16	-0.52
0.1953	323.22	2.485	0.034	2.499$^{(b)}$	-0.14	-0.57
0.2043	292.96	1.390	0.023	1.390$^{(a)}$	0.00	-0.02

(a) Arami-Niya *et al.* (2020).
(b) Juntarachat *et al.* (2014).

3. RESULTS AND CORRELATION OF DATA

Bubble point pressures for the R-290 + POE ISO 32 four molar compositions (approximately 0.2015, 0.4021, 0.6009 and 0.8003) of R-290 were measured from 283.15 to 343.15 K. The results for each composition are reported in Table 4.

Table 4. Measured bubble point pressures, *p*, for the system R-290 (1) + POE ISO 32 (2) at temperature *T* and liquid mole fraction x_1 .

x_1=0.2015 ±0.0083				x_1=0.6009 ±0.0045			
T [K]	P [MPa]	U(*p*) [MPa]	(U(*p*)/p) x 100	T [K]	P [MPa]	U(*p*) [MPa]	(U(*p*)/p) x 100
283.07	0.128	0.029	22.7	283.10	0.377	0.026	6.9
298.13	0.163	0.030	18.4	298.06	0.558	0.027	4.8
313.17	0.208	0.030	14.4	312.81	0.765	0.028	3.7
328.20	0.270	0.030	11.1	328.20	1.040	0.030	2.9
343.16	0.331	0.031	9.4	343.07	1.345	0.030	2.2
283.17	0.130	0.029	22.3	283.00	0.380	0.027	7.1
x_1=0.4021 ±0.0067				x_1=0.8003 ±0.0041			
T [K]	P [MPa]	U(*p*) [MPa]	(U(*p*)/p) x 100	T [K]	P [MPa]	U(*p*) [MPa]	(U(*p*)/p) x 100
283.20	0.237	0.028	11.8	283.31	0.564	0.028	5.0
298.18	0.337	0.029	8.6	298.13	0.825	0.030	3.6
313.17	0.461	0.029	6.3	313.10	1.175	0.030	2.6
328.09	0.610	0.031	5.1	328.12	1.624	0.030	1.8
343.11	0.782	0.032	4.1	343.10	2.174	0.032	1.5
283.27	0.245	0.028	11.4	283.24	0.563	0.027	4.8

The data were correlated with two equations of state, Peng and Robinson (1978) - called PR in this article - and PC-SAFT (Gross and Sadowski, 2001). The PR equation is a modified cubic equation of state based on the van der Waals equation of state. To this day the PR equation of state is still used due to its reasonable prediction capacity, simplicity, and computational efficiency (Span, 2000). The PC-SAFT equation was proposed by Gross and Sadowski (2001) and it is based on the statistical associating fluid theory (SAFT), by applying the perturbation theory of Barker and Henderson (1967) to a hard-chain reference fluid (Assael *et al.*, 1996). The PC-SAFT equation has been successfully applied to model phase equilibria of complex systems, including refrigerant + lubricant mixtures (Marcelino Neto and Barbosa Jr., 2014b; Fouad *et al.*, 2019; Czubinski *et al*., 2020).

The PR equation requires only the critical pressure (p_c) and critical temperature (T_c), and the acentric factor (ω) for its application to a pure fluid. In the PC-SAFT equation, three pure component parameters are required: the number of segments per chain (m), the segment diameter (σ) and the depth of the pair potential (ε) (Assael *et al.*, 1996). For R-290, the parameters of PR and PC-SAFT equation were taken from Lemmon et al. (2013) and Gross and Sadowski (1999), respectively. For POE ISO 32, these parameters were obtained by fitting to the experimental density data available in Morais *et al.* (2020), in a similar fashion reported by several authors (Huber *et al.*, 2002; Fandiño *et al.*, 2010; Fouad *et al.*, 2019). Pure fluid parameters and the corresponding molecular weights (*MW*) are reported in Table 5.

Table 5. Parameters for the PR and PC-SAFT equations of state for pure fluids.

Fluid	*MW* [g/mol]	T_c [K]	p_c [MPa]	ω [-]	ε/ κ [K]	σ [˚A]	*m* [-]
R-290	44.10	369.89	4.251	0.152	208.11	3.6184	2.002
POE ISO 32	560.26(1)	597.19	7.663	0.427	321.98	4.6021	8.747

(1) Morais *et al.* (2020).

Once the pure components parameters are available, the equations of state can be used to study the behavior of their mixtures. In both equations, the cross-energy interaction terms (a_{ij} and ε_{ij}) were obtained using a geometric mixing rule with an adjustable parameter, k_{ij} :

$$a_{ij}=\left(a_i a_j\right)^{0.5}\left(1-k_{ij}^{PR}\right) \tag{1}$$

$$\varepsilon_{ij}=\left(\varepsilon_i \varepsilon_j\right)^{0.5}\left(1-k_{ij}^{SAFT}\right) \tag{2}$$

where a is attractive term which depends on the critical parameters and acentric factor. A simple mixing rule was used for the cross-size parameters:

$$b_{ij}=\left(b_i+b_j\right)/2 \tag{3}$$

$$\sigma_{ij}=\left(\sigma_i+\sigma_j\right)/2 \tag{4}$$

The binary interaction parameters, k_{ij}^{PR} and k_{ij}^{SAFT}, can be obtained by direct fitting the models to experimental data, minimizing the following objective function:

$$\Delta \mathrm{p} = \sum_{\mathrm{i}=1}^{\mathrm{n_p}} \left| \frac{p_i^{cal} - p_i^{exp}}{p_i^{exp}} \right| \tag{5}$$

where p_i^{cal} and p_i^{exp} correspond to the calculated and experimental bubble point pressure.

Figure 2 presents the pressure-composition isotherms for the mixtures obtained using the PR and PC-SAFT. The bubble point pressures for this mixture are represented with average absolute deviation (AAD) of 5,89% and 4,63% using PR and PC-SAFT equations of state, respectively. The value of the binary interaction parameters k_{ij}^{PR} was –0.0404 and k_{ij}^{SAFT} was equal to 0.0424. Bubble point pressure increases with the temperature increasing at a fixed molar fraction. As expected, the molar fraction of R-290 increases when the pressure increases at a fixed temperature. As can be seen, only vapor-liquid phase equilibrium was observed for the mixture for the studied range of temperature and composition.

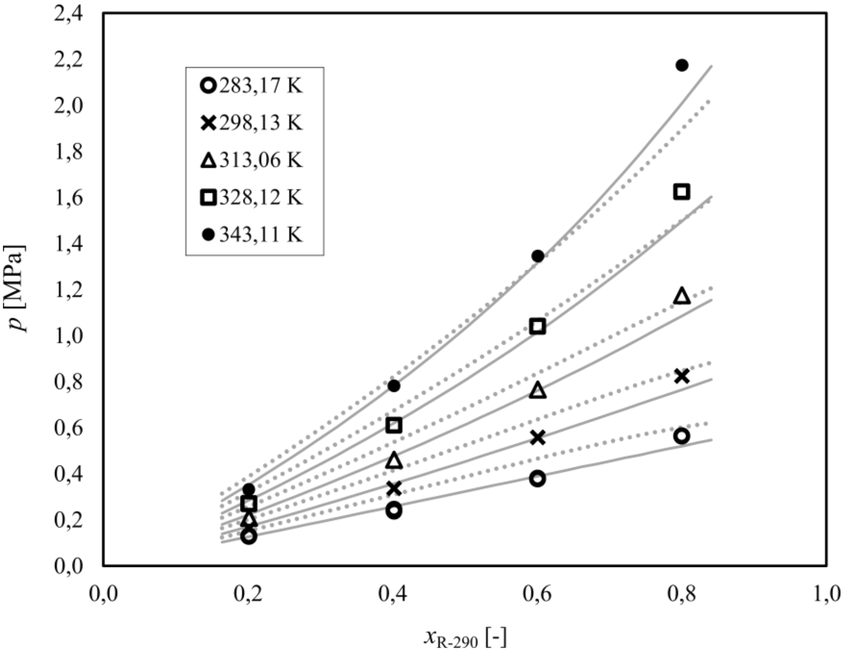

Figure 2. Experimental bubble point pressures for R-290 + POE ISO 32 mixture. Solid curves correspond to PC-SAFT equation results and dotted curves correspond to PR equation of state.

The relative uncertainty (defined as the total uncertainty divided by the measured bubble point pressure) is reported in percentage for each bubble point pressure measurement. As seen in Figure 3, the relative uncertainties are larger for low temperatures and small mole fractions of R-290.

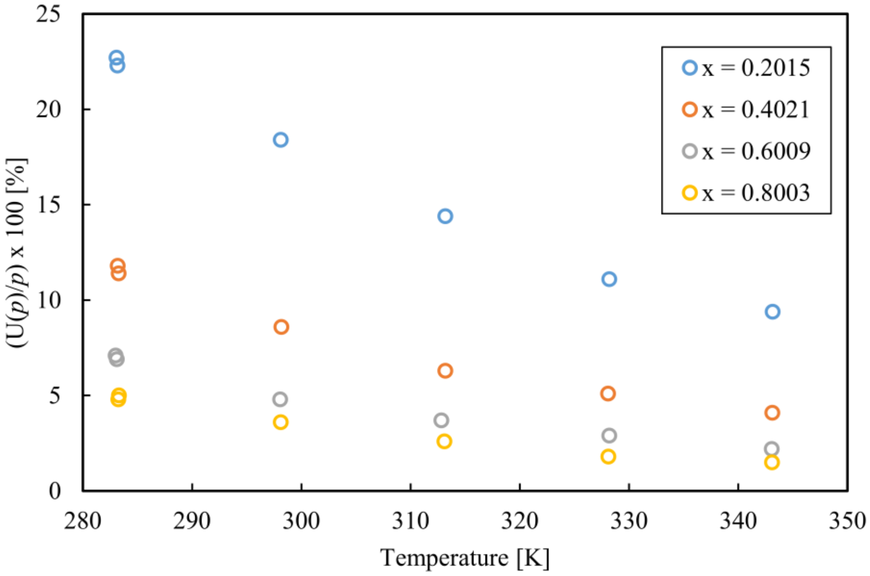

Figure 3. Relative uncertainty of experimental bubble-point pressures for R-290 + POE ISO 32 mixture.

4. DISCUSSION AND CONCLUSIONS

A total of 24 bubble point pressure were measured for the system R-290 + POE ISO 32 at temperatures from 283.15 to 343.15 K. Measurements of bubble point pressure for the R1234yf + CO2 mixture and pure propane demonstrate the validity of the experimental procedure. It was verified that R-290 is completely miscible with POE ISO 32 in the range of temperature and composition studied. The experimental data were correlated with the Peng and Robinson (1978) equation with an AAD = 5.89%, and with the PC-SAFT model (Gross and Sadowski, 2001) with an AAD = 4,63%. The results have been used to obtain optimized binary parameters for the Peng–Robinson and PC-SAFT equations of state. Finally, the experimental measurements presented here expand the thermodynamic property database for refrigerant + oil lubricant mixtures.

5. ACKNOWLEDGEMENTS

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