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## INVESTIGATION OF THE THERMOPHYSICAL PROPERTIES OF THE R744 + R1234YF BINARY SYSTEM

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### ABSTRACT

In 2014, European F-gas directive plans the prohibition of fluorinated working fluids with GWP of 2500 or more from 2020. Consequently, new working fluids have to be considered in the future such as HydroFluoroOlefin, carbon dioxide or mixture of HFO with hydro-fluoro-carbon or CO<sub>2</sub>. The knowledge of the thermo-physical properties of working fluid is essential for the evaluation of performance of heat pumps, ORC and refrigeration. Herein, several “French” laboratories proposed to investigate the thermo-physical properties of the R744 + R1234yf binary system. In 2014, Juntarachat et al. measured and correlated vapour liquid equilibria including mixture critical point. New experimental determinations for density and viscosity using vibrating densitometer and capillary viscometer are presented. Also, enthalpies of mixing are determined using BT-215 Calvet calorimeters. In addition, molecular simulation based on empirical force have been realized. Several thermodynamic and transport properties have been obtained using Monte Carlo and Molecular Dynamics simulations. The PPR78 cubic equation of state and a multipolar version of SAFT-Mie are used to predict the new experimental data for thermodynamic properties. The model developed is used as an input to simulate the performance of new heat pump system. An experimental heat pump is used to evaluate the achievable energy efficiency with this mixture in real machines with one test molar composition of 5% R1234yf). The optimal pressure and COP will be compared to those obtained with pure CO<sub>2</sub> in similar operating conditions.

**Keywords:** R1234yf, CO<sub>2</sub>, experimental VLE data, calorimetry, transport properties, PPR78 model, molecular simulation.

## 1. INTRODUCTION AND SCIENTIFIC OBJECTIVES

Recently, following conclusion of Kigali conference in October 2016, it was admitted that hydrofluorocarbons (HFC's) are banned for utilisation in refrigeration. This is the consequence of an environmental policy started in 1985 with Montreal Protocol. The F-gas regulations were created in order to plan the utilisation and replacement of these refrigerants. The 2009 F-gas regulation (Regulation (EC) [1] revised in 2014) fixes the limits of GWP for each year. In order to reach the objectives in terms of GWP, two solutions exist: the first one consists in developing new fluids with low GWP values, such as hydrofluoroolefines (HFO's). The second one consists in developing new blends of refrigerants (less than 3 components).

The development of refrigerators, heat pumps or organic Rankine cycle machines requires the knowledge of the thermodynamic properties and the phase diagram of fluids. The selection of working fluid is based on the determination of performance coefficient or energy efficiency of the systems. Also, for the design of heat exchangers with and without phase change, it is necessary to know the state of the fluid and to evaluate the level of the temperature or pressure glide. In this case, it is important to know if the fluid behaves like a pure component (azeotropic behaviour) or not. Additionally, the selection of the oil of the compressor requires the knowledge of the upper critical end point temperature (temperature of apparition of liquid liquid demixion).

Thermophysical properties are also essential for the design of the heat exchangers. Chemical engineers use correlations with dimensionless numbers (with Nu, Re and Pr, respectively, Nusselt, Reynolds and Prandtl numbers) to estimate heat transfer coefficient essential for the estimation of global heat transfer coefficient of the heat exchanger.

The thermodynamic properties are obtained by using equations of state (EoS's). In the process simulators, the most famous EoS's are of cubic type. Other type of equation of state of molecular type can be used. The Helmholtz energy is calculated by considering all the molecular interactions like dispersion, polarity, H bonding (association), etc... The most known molecular EoSs of this type are SAFT type (Chapman et al. [2]) using Wertheim's statistical theory of associative fluids (Wertheim [3]). The various versions differ mainly in the choice of the reference fluid, the radial distribution function and explicit expressions of the terms of perturbation.

In this communication, we proposed to investigate the thermophysical properties of the binary system CO<sub>2</sub> + R1234yf and evaluation of performance of a cycle of refrigeration. We have compared experimental data with molecular simulation predictions. Some experimental data are correlated by two EoS: PPR78 and SAFT Mie EoS.

## 2. DESCRIPTION OF EXPERIMENTAL TECHNIQUES

In this section, we will present several apparatuses used for the experimental determination of thermodynamic and transport properties.

### 2.1. Equilibrium properties and critical point

Vapour - liquid equilibrium properties can be obtained using the "static analytic" method. Herein, the mixture is enclosed in an equilibrium cell equipped with a mixing mechanism to get fast equilibrium conditions. When the equilibrium is reached, small quantities of the phases are sampled and analyzed through chromatographic analyzers. Complete descriptions of the setups are available in Juntarachat et al. [4]. Concerning critical point measurement, another equipment is used. It is a synthetic method where the mixture is circulating through the equilibrium cell under specific conditions of temperature and pressure. A critical point can be determined by visually observing the critical opalescence and the simultaneous disappearance and reappearance of the meniscus i.e. of the liquid-vapor interface in the middle of the view cell.

### 2.2. Viscosity

Viscosities of CO<sub>2</sub>, R1234yf and their mixture was measured using the capillary tube viscosity method. This setup has been designed to have a maximum working pressure of 200 MPa between 243.15 to 523.15K. The set-up is comprised of two small cylinders, with volumes of 25 cm<sup>3</sup>, connected to each other through a capillary tube with measured length of 14.78 metres and a temperature-dependent calibrated internal diameter. A

complete description of this technique is available in the paper of (Kashefi et al. [5]). The temperature of the system was set to the desired condition and the desired pressure was set using the hand pump. Poiseuille equation (Eq. 1) (in laminar flow conditions) can relate the pressure drop across the capillary tube to the viscosity, tube characteristics and also flow rate for laminar flow.

$$\Delta P = \frac{128LQ\mu}{C\pi D^4} \quad (1)$$

where,  $\Delta P$  is the differential pressure across the capillary tube viscometer in psi,  $Q$  represents the flow rate in cm<sup>3</sup>/sec,  $L$  is the length of the capillary tube in cm,  $D$  refers to the internal diameter of the capillary tube in cm equals 0.029478 cm,  $\mu$  is the viscosity of the flown fluid in cP and  $C$  is the unit conversion factor equal to 6894757 if the above units are used.

### 2.3. Enthalpies of mixing

Measurements have been performed using a customized BT2.15 calorimeter from Setaram, France. The calorimeter cooling system was modified to operate using liquid circulating fluid at sub-ambient conditions instead of liquid nitrogen as a cooling agent. Arcis et al. [6] present the experimental setup and the procedure used. The two fluids are injected in the calorimeter mixing unit using two high pressure syringe pumps. Before entering the calorimeter, the fluids are refrigerated when circulating through an external pre-cooler, which is controlled at temperature 10 degrees below temperature of calorimeter. A pre-heater is inserted inside the calorimeter. This preheater is surrounding the fluids entering tubing in order to adjust accurately the temperature of the fluids to the temperature of the calorimetric bloc. The pressure is maintained constant using a buffer volume, while its value is obtained using a Keller pressure transducer (P). The low temperature calorimetric device was tested using the mixture {Heptane + Toluene} at 283.3 and 263.15 K. The experimental excess enthalpies were compared to literature values (Holzhauer and Ziegler [7]), and the average standard deviation was found to be 1.0%.

## 3. MODELING

### 3.1. Molecular simulation

More details concerning the methods used will be explain in section 5.2. The main goal of molecular simulation is to help the selection of fluids by a “fast” estimation and comparison of the thermophysical properties. The data obtained with any experimental work will be used by thermodynamic models to test the efficiency of the fluids.

### 3.2. Cubic Equation of state: PPR78

Our data were correlated with the well-established 1978 version of the Peng-Robinson equation of state (EoS) [8], referred as PR78 in this paper. The model is fully described in the paper of Juntaratchat et al. The PPR78 model is based on the PR78 EoS using Classical van der Waals one-fluid mixing rules. The  $k_{ij}(T)$  parameter, whose choice is difficult even for the simplest systems, is the so-called binary interaction parameter (BIP) characterizing the molecular interactions between molecules  $i$  and  $j$ . In this study, the temperature dependence of the  $k_{ij}$  was determined following the equations developed for the PPR78 [9] models (Eq. 2).

$$k_{ij}(T) = \frac{-\frac{1}{2} \left[ \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \cdot \left( \frac{298.15}{T/K} \right)^{\left( \frac{B_{kl}}{A_{kl}} - 1 \right)} \right] - \left( \frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \sqrt{\frac{a_i(T) \cdot a_j(T)}{b_i \cdot b_j}}} \quad (2)$$

Eq. 2 highlights that one needs to estimate two constant parameters ( $A_{12}$  and  $B_{12}$ ) for each binary system. VLE data published in the open literature as well as our own data measured in the present study were used to determine the optimal values of these parameters. All the results and details concerning objective function and values of  $A_{12}$  and  $B_{12}$  parameters are presented in the paper of Juntaratchat et al.

### 3.3. Multipolar SAFT-Mie Model

The recently proposed multipolar SAFT-Mie model (Glorian et al. [10]) is used to predict the VLE and thermodynamic properties of the CO<sub>2</sub>+R1234yf mixture. The M-SAFT-Mie EoS is a molecular model that takes explicitly into account dispersion and electrostatic interactions. It is a combination of the SAFT-Mie EoS (Lafitte et al [11]) with the multipolar term developed by Gubbins and co-workers (Gray et al. [12]). The dispersion interactions are described by Mie potentials while electrostatic interactions are represented with point dipoles and quadrupole: CO<sub>2</sub> is modeled as a quadrupolar molecule while R-1234yf has both a dipole and a quadrupole. The SAFT parameters of CO<sub>2</sub> and R1234yf are fitted to both pure component properties (vapor pressures, liquid densities, vaporization enthalpies, heat capacities and speeds of sound) and VLE data of mixtures with alkanes.

## 4. DESCRIPTION OF THE EXPERIMENTAL HEAT PUMP

The performance assessment of mixtures as a working fluid is performed on a complete heat pump loop. This bench is based on a water to water single stage CO<sub>2</sub> heat pump, built up with commercial R-744 components: variable speed scroll compressor, brazed plate gas cooler, brazed plate evaporator, internal heat exchanger with liquid receiver and an electronic expansion valve. The heat pump loop supplies from 2 to 5 kW of heat output. It is instrumented with thermocouples (carefully recalibrated in our lab), pressure transmitters, two Coriolis flow meters (for both the high and low pressure sides of the cycle), a wattmeter, five “in-line” optical flow-cells for near infra-red spectra measurements and 3 micro-samplers for gas chromatography analysis of the circulating refrigerant mixture. The Coriolis flowmeters allow both mass flowrate and density measurements. The near infrared spectra are used to determine the composition of the circulating mixture and gas chromatography is used to calibrate the optical composition measurement method. Therefore, with this facility, COP and fluid composition measurements can be carried out simultaneously. A more detailed description is given elsewhere (Bouteiller et al. [13]).

## 5. PRESENTATION OF SOME RESULTS AND CONCLUSIONS

### 5.1. Equilibrium properties and viscosities

The isothermal (P-x-y) vapor-liquid equilibrium data of the CO<sub>2</sub> (1) + R1234yf(2) binary system, measured at seven temperatures (283.15 + 293.15 + 298.15 + 308.15 + 323.15 + 338.15 + 353.15) K using the static-analytic type apparatus. The experimental critical values for the CO<sub>2</sub> (1) + R1234yf(2) binary system and their modeling at different mole fractions were also determined. The PPR78 EoS combined with a temperature-dependent binary interaction parameter was used to correlate the subcritical and critical phase behavior of the considered systems. Fig. 1 illustrates the comparison between the experimental VLE data measured in this work, literature data (Di Nicola et al. [14-15]) and correlated values with the PR78 model for the CO<sub>2</sub>(1) + R1234yf(2) binary system.

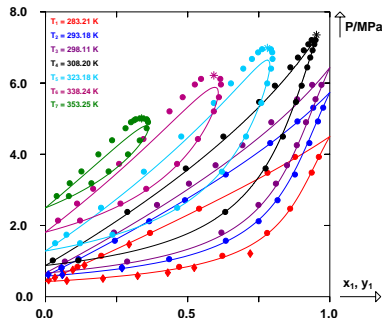


Fig. 1. P-x-y phase diagram for CO<sub>2</sub>(1) + R1234yf(2) binary system at seven temperatures, Symbols: experimental data (Juntaratchat et al. and Di Nicola et al.), solid lines: PR78 EoS

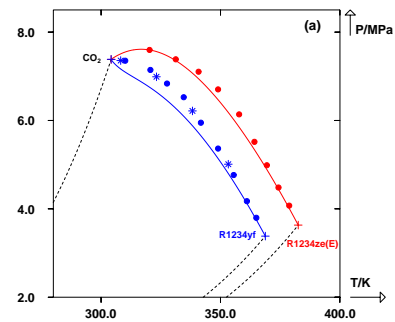


Fig. 2. Comparison between experimental and calculated critical values (P-T projection) and correlation with the PR78 model. Symbols: Juntaratchat et al., lines: PR78 model.

A good agreement is obtained between our experimental data and those collected by Di Nicola et al. [14-15] at temperatures 283.15 and 293.15 K. It is observed that the PR78 EoS is capable of accurately correlating the experimental bubble and dew points at temperatures up to 308.15. The model however loses its modeling

capacity at higher temperatures, particularly for bubble points in the critical region. As explain in [4] the addition of a second binary interaction parameter on the co-volume mixing rule could certainly bring a solution to this problem. Both of the studied systems display a continuous liquid-vapor critical locus which connects the critical points of the pure substances (Fig. 2). Consequently, such mixtures exhibit type I or type II phase behavior in the classification scheme of Van Konynenburg and Scott [16]. The PR78 EoS predicts a type II for the CO<sub>2</sub> + R1234yf system. Fig. 3 and Fig. 4 present the results obtained on viscosity measurements. Deviations are observed with REFPROP predictions.

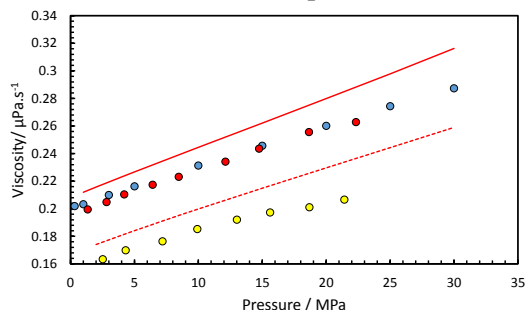


Fig. 3. Viscosity of R1234yf and the binary 0.7969 R1234yf + 0.2031 CO<sub>2</sub> system at 273.15 K. (●) R1234yf data from Meng et al. [17]; (●) R1234yf this work; (●) R1234yf + CO<sub>2</sub> this work; Red lines: predictions using REFPROP.

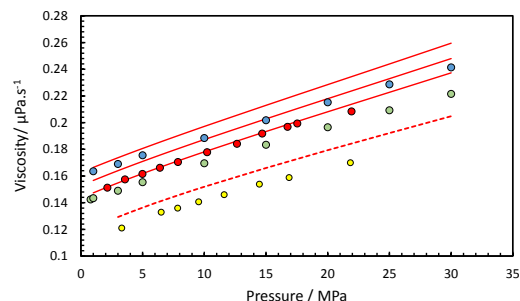


Fig. 4. Viscosity of R1234yf and the binary 0.7969 R1234yf + 0.2031 CO<sub>2</sub> system at 293.15, 298.15 and 303.15 K. (●) R1234yf data from Meng et al. at T=293.15 K; (●) R1234yf data from Meng et al. at T=303.15 K; (●) R1234yf this work at 298.15 K; (●) R1234yf + CO<sub>2</sub> this work at 298.15 K; Red lines: predictions using REFPROP

## 5.2. Molecular simulation and M-SAFT-Mie modeling

We have produced two types of molecular simulation data for the mixture CO<sub>2</sub>+R1234yf: isothermal vapor-liquid equilibrium data and mixing and transport properties at given temperature and pressure. In both cases, we used the force field from (Potoff and Siepmann [18] for CO<sub>2</sub> and of Raabe and Maginn [19] for HFO-1234yf. The force field for CO<sub>2</sub> was optimized in order to reproduce quantitatively the vapor-liquid equilibria of pure CO<sub>2</sub> and CO<sub>2</sub>-alkane mixtures. The liquid-vapour equilibrium data of pure compounds and binary mixtures were obtained with Monte Carlo (MC) simulations using the GIBBS Monte Carlo code (Ungerer et al. [20]), apart from the P-x-y data at 273 K which were obtained by using the Towhee code. These simulations were performed in the Gibbs NVT ensemble for the pure compounds (constant number of particles N, constant total volume V and constant temperature T) and Gibbs NPT ensemble for the mixtures (constant number of particles N, constant pressure P and constant temperature T) (Panagiotopoulos [21]). We present on Fig. 5 the P-x-y plot for CO<sub>2</sub>+R1234yf at 283.21K and 273.15K. The simulation data at 283.21 K are compared with experimental values from [4]. The bubble curve is particularly well reproduced. The overall agreement with the dew curve is good. From these simulations, we were able to extract the vaporization enthalpy  $\Delta H_{vap}$ , shown on Fig. 6. Molar enthalpy of both phases were plotted versus composition and fitted using a linear regression.  $\Delta H_{vap}$  was computed as the difference between the phase enthalpies at a given composition. To our knowledge, there is no experimental data available at 273.15 K.

Enthalpies of mixing were obtained using the standard relation  $\Delta H_{mix}(P,T) = H(P,T) - \sum x_i H_i^*(P,T)$ . We obtain a positive enthalpy of mixing, as shown on Fig. 7. It should be mentioned that the absolute value of  $\Delta H_{mix}$  is quite small, of the order of a 100 Joules per mol. Volumes of mixing are even smaller, of the order of 0.2% of the system volume.

The VLE of the CO<sub>2</sub> + R1234yf is predicted considering M-SAFT-Mie model with classical mixing rules and binary parameters ( $k_{ij}$ ) equal to zero. As shown in Fig. 1, the model accurately predicts the experimental VLE data at 283.21K and is in perfect agreement with the molecular simulation data at 273.15K. The predicted enthalpies of mixing are of the same order of magnitude and sign as the experimental data; however, the maximum mixing enthalpy is over predicted by M-SAFT-Mie (Fig 7).

The second set of simulations was designed to obtain thermal conductivity of the CO<sub>2</sub>+R1234yf mixtures at 283.15 K and a pressure of 6 MPa. First, Monte Carlo simulations in the NPT ensemble were realized to obtain the equilibrium density of each mixture. Large boxes with 2000 molecules were considered. Then, molecular dynamics simulations were realized and thermal conductivity was computed using non-equilibrium molecular dynamics (NEMD) and the HeX algorithm (Hafskjold [22]). Thermal conductivity is

presented on Fig. 8. To our knowledge, there is no available data for the thermal conductivity of HFO-1234yf under the conditions studied here. Thermal conductivity has been measured along the liquid-vapor equilibrium by (Saitoh et al. [23]) at 288.15 K. We obtained  $\lambda=72.4 \text{ mW m}^{-1}\text{K}^{-1}$  was obtained. At this state point, the density value is  $1077.3 \text{ kg m}^{-3}$ , much lower than the density under 6 MPa used here. As thermal conductivity is expected to increase with density, the value obtained using molecular dynamics might be a good estimate for HFO-1234yf. The thermal conductivity prediction for pure  $\text{CO}_2$  is 5% higher than the one obtained by (Vesovic et al. [24]).

The surface tensions of the 1:4  $\text{CO}_2/\text{R1234yf}$  mixture in the temperature range 273.15-298.15 K were computed from the test-area method (Gloor et al. [25]). The molecular dynamics simulations were performed using the code POLARIS(MD) at the 5 ns scale. The integration time step was 0.5 fs. The surface tension long range corrections were computed from a standard formula (Vega et al. [26]), in which the liquid/vapor interface thickness was estimated from the profile of the mean molecular density along the axis orthogonal to the interface. From Fig. 9, we can see that the molecular simulation results are in good agreement with the REFPROP results, with a maximum relative error of 5% at 273.15 K.

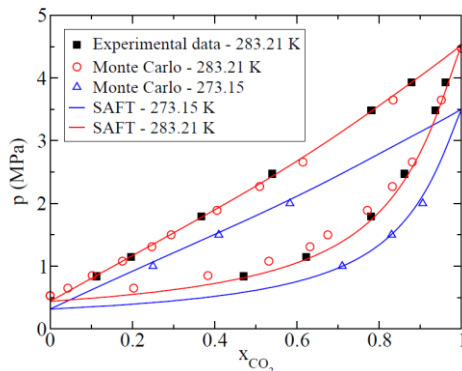


Fig. 5: P-x phase diagram for  $\text{CO}_2+\text{R1234yf}$  mixture. Red dots : Monte Carlo simulations, black square : experimental data from [4]. Solid lines: M-SAFT-Mie predictions

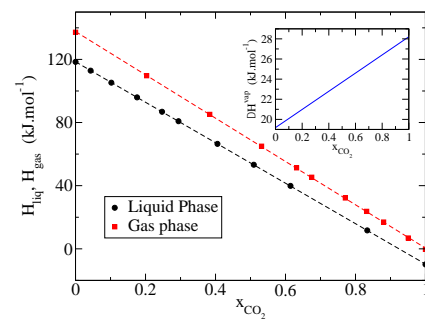


Fig. 6: Molar enthalpies versus composition for the liquid and gas phases of  $\text{CO}_2+\text{R1234yf}$  mixtures at 283.21 K. Insert : Vapourisation enthalpy versus composition

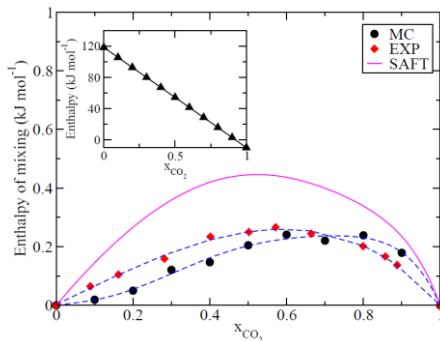


Fig. 7 : Excess enthalpies of  $\{ \text{CO}_2+\text{R1234yf} \}$  mixture at 283.3 K and 6 MPa. Comparison between experimental data and molecular simulation data. Line are guides to the eyes. Solid lines: M-SAFT-Mie predictions. Insert : total enthalpy of the mixture versus composition from molecular simulation.

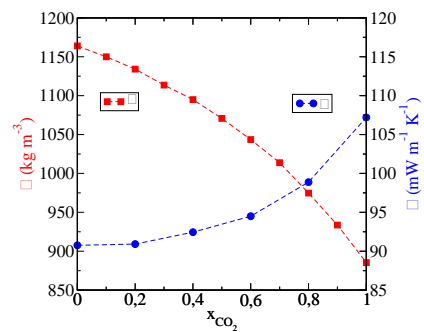


Fig. 8: Thermal conductivity and density of the  $\text{CO}_2+\text{R1234yf}$  obtained from molecular simulation at 283.15 K and 6 MPa

### 5.3. Experimental determination of calorimetric properties

The first measurements have been carried out at temperatures 263.3 K and 283.3 K and at 1.0 MPa. at this pressure,  $\text{CO}_2$  is gas and R1234yf is liquid and heat effects are related to an enthalpy of solution of  $\text{CO}_2$  in R1234yf. The enthalpies of solution obtained (12.0 and 13.5  $\text{kJ/molCO}_2$  at 263.15 K and 283.3 K respectively) are in order of magnitude of values observed for a physical dissolution of the gas in the liquid.

Second experiments have been performed at 263.15 K and at 6.0 MPa. Both fluids are in liquid phase and the enthalpy is an excess molar enthalpy. The excess enthalpy at 283.3 K and 6.0 MPa is represented as function of  $\text{CO}_2$  molar fraction in Fig. 7.

The excess molar enthalpies show endothermic effect with a maximum observed around CO<sub>2</sub> molar fraction of 0.6. Those results are consistent with the values estimated using molecular dynamics simulations presented before.

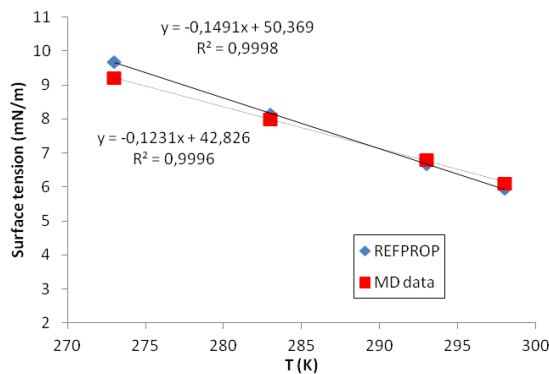


Fig. 9: Surface tension of the 1:4 CO<sub>2</sub>/R1234yf mixture from molecular dynamics and from REFPROP

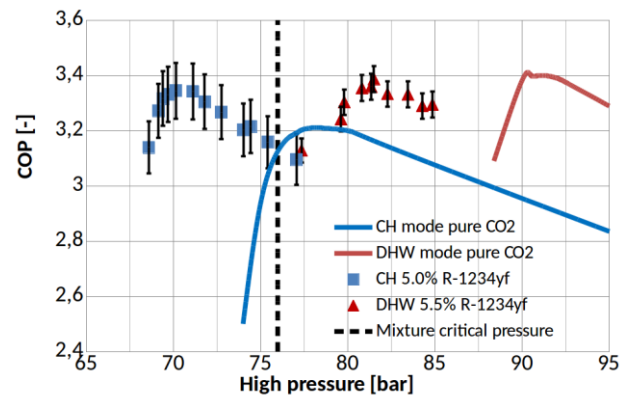


Fig. 10: Heat pump loop and experimental bench and performances with a CO<sub>2</sub> + R-1234yf mixture compared to pure CO<sub>2</sub> performances

#### 5.4. Mixture test in a heat pump loop

Two working modes for the heat pump are considered here: CH: Central Heating, where water is heated from 30 to 35°C and DHW: Domestic Hot Water, where water is heated from 10 to 65°C. For both modes, the brine temperature at the evaporator inlet is kept constant at 7°C. This accounts for temperate climate conditions. It is well known that for pure CO<sub>2</sub> trans-critical cycles, a maximum COP is obtained at a given optimal high pressure (Liao et al [27]). This is shown on Fig. 10 which shows a plot of the COP, versus the high pressure level of the heat pump. The Fig. 10 also shows the results with one CO<sub>2</sub> + R-1234yf mixture that was introduced in the heat pump. Measured mole fractions of the circulating mixture are about 5.5 % of R-1234yf for the Domestic Hot Water (DHW) mode and 5.0 % for Central Heating (CH) mode. It can be clearly seen on the plot that for both working modes, the working pressures with the mixture are reduced compared to those with pure CO<sub>2</sub>. A comparison of maximum COP shows that although, no performance enhancement can be observed for DHW mode, higher COPs were achieved for CH mode with the mixture than with pure CO<sub>2</sub>. Notice that for the latter case, most of the cycles are no more trans-critical. For those cycles, the pressure in the high temperature exchanger is lower than the mixture critical pressure (73.6 bar) as shown on the Fig. 10. This means that condensation occurs in this exchanger. The maximum COP is obtained for such a subcritical cycle. Such encouraging results lead us to the conclusion that more research on mixtures properties would be beneficial for the refrigeration and heat pump industry.

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