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Alaa Hajlaoui, Laurène Salat, Laurence Rodier, Jean-Michel Andanson, Yohann Coulier. Thermodynamic study of working fluid pairs for an absorption refrigeration process. International Conference of Refrigeration, Aug 2023, Paris, France. hal-04224702

HAL Id: hal-04224702

<https://hal.science/hal-04224702v1>

Submitted on 2 Oct 2023

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Thermodynamic study of working fluid pairs for an absorption refrigeration process

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ABSTRACT

Vapor-absorption refrigeration technology has received growing attention in the past years for its numerous advantages especially in connection with energy efficiency. In this technology the pressure variations are related to absorption/desorption cycles of the refrigerant in the absorbing solution. Our goal is to explore a radically different path regarding the search of new natural refrigerant/absorbent pairs. To limit the environmental impact of the working fluid pairs, the natural refrigerant investigated is carbon dioxide (CO₂) and the absorbent is a bio-based solvent (BBS).

In order to improve and modify the vapor absorption process, one must know the thermodynamic and volumetric properties of the working fluids since they highly influence the performance of the absorption cycle. In the absorber and generator, enthalpy of solution and vapor equilibrium data are the major process variables. The knowledge of density is also important.

This work presents the energetic and volumetric properties determined experimentally of {CO₂ + BBS} system using four different absorbents namely propylene carbonate, anisole, γ -valerolactone, and cyrene. Comparisons between our experimental data and literature data confirm the accuracy of our measurements and its capacity to fit thermodynamic models.

Keywords: Refrigeration, Carbon Dioxide, Biobased solvent, absorption.

Refrigeration systems are an essential technology in domestic and industrial sectors. Currently, the most widely used refrigeration system is the vapor compression cycle (VCR). It includes at least 4 essential elements (the compressor, the condenser, the expansion valve, and the evaporator) in which the refrigerant circulates and undergoes phase changes in order to absorb the heat from the space in the evaporator and then reject it in the condenser.

The most widespread refrigerants are hydrofluorocarbons (HFC). However, these working fluids are concerned by short or mid-term prohibitions regarding their environmental impact since they contribute to global warming. According to the International Institute of Refrigeration (IIR) (Coulomb et al., 2017), the refrigeration sector (including air conditioning) consumes about 17% of the overall electricity used worldwide and accounts for 7.8% of global greenhouse gas emissions. Of these emissions 63% indirect emissions related to the production of the electricity consumed by refrigeration systems and 37% are direct gas emissions due to refrigeration leaks during maintenance or operation of refrigeration machines.

To overcome the environmental problems and to cope with the rapid growth in energy demand associated with the conventional compression refrigeration systems, vapor-absorption refrigeration technology is of interest. In this case, the compressor of the VCR is replaced by a pump, a boiler, and an absorber. The

pressure variations are related to the absorption/desorption cycles of the refrigerant in an absorbing solution. This technology has received growing attention in the past years thanks to its advantages such as the use of the renewable energies (residual heat recovered from industrial processes or heat supplied by renewable sources) and zero ozone depletion potential (ODP) working fluid pairs ($\text{H}_2\text{O}/\text{LiBr}$ or $\text{NH}_3/\text{H}_2\text{O}$). However, in addition to their poor thermodynamic properties that result in a low coefficient of performance (COP), these fluids exhibit specific drawbacks such as technological challenges, or health hazards, or environmental concerns which prevent wider use (Srikhirin et al., 2001; Sun et al., 2012).

It should be mentioned that the thermodynamic and physicochemical properties of the absorbent/refrigerant pair are of great importance in absorption refrigeration machines as they strongly influence the efficiency of the process (Coquelet et al., 2016; Perez-Blanco, 1984). As shown in Fig. 1, these properties should be measured at sub-ambient condition of pressures and temperatures. In the absorber, enthalpy of solution ($\Delta_{\text{sol}}H$) and VLE data are the major process variables and, in the generator, the heat required to separate the CO_2 from the absorbent is the opposite of enthalpy of solution at temperature and pressure conditions. Knowing the volumetric and thermal capacity data allows optimization of the liquid pump and solution heat exchanger performance. Besides the enthalpies of mixing of CO_2 +BBS systems are crucial parameters for simulating VAR cycle performances. Finally, BBSs must be very stable over a wide operating temperature range.

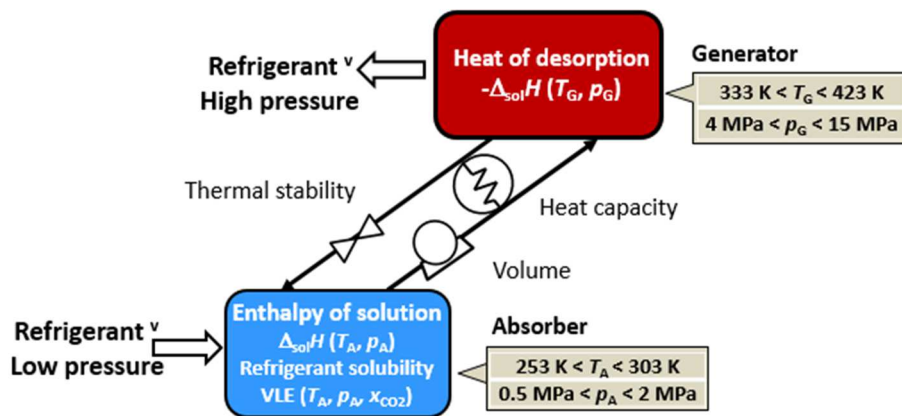


Figure 1. Key thermodynamic parameters for the representation of the absorption/separation unit.

Many research have been carried out to improve the absorption refrigeration technology by changing the design parameters (Karamangil et al., 2010), improving currently used working fluid pairs (Macriss et al., 1988; Sun et al., 2012) or proposing new ones (Khan et al., 2022; Macriss et al., 1988; Nikbakhti et al., 2020; Srikhirin et al., 2001; Sun et al., 2012).

The most important considerations when selecting an appropriate working fluid pair are:

- Strong affinity between the absorbent and the refrigerant at the operating conditions of the absorber;
- much more volatility of the refrigerant than the absorbent;
- low heat of mixing of absorbent and refrigerant;
- non-corrosive, favorable mass and heat transfer;
- no solidification or crystallization
- cost-effective and environmentally friendly.

To promote this technology, our work focuses on the investigation of new potential natural refrigerant/absorbent pairs. In order to limit the environmental impact, we have selected carbon dioxide (CO_2) as the natural refrigerant. It is one of the few natural non-toxic and non-flammable refrigerants. It is cheap and largely available with a low environmental impact (ODP=0 and GWP=1) (Lorentzen, 1994). In

addition, CO₂ has key advantages in refrigeration applications, including high latent heat and thermal conductivity. The absorbent will be a bio-based solvent with low volatility and strong affinity to the former. In this case, the conditions of high temperature and pressure will lead to the use of a CO₂ transcritical cycle. For this reason, the condenser will be replaced by a gas cooler.

Using a precise methodology, described in our previous work (Coulier et al., 2022), more than twenty BBSs were identified. Five of them have been studied in the last article (Coulier et al., 2022) namely ethyl levulinate, anisole, dibutyl succinate, γ -butyrolactone, and cyrene. Based on experimental data from literature and our work (for cyrene), we were able to select an appropriate thermodynamic model capable of reproducing phase equilibria and thus comparing the CO₂ solubility in these five BBSs at 283 and 353 K.

To continue the work we have already achieved, the present study aims to report some experimental measurements of calorimetric and transport properties performed on four chosen {CO₂ + BBS} systems. The solvents that will be presented in this paper are propylene carbonate (PC), anisole (ANI), γ -valerolactone (GVL), and cyrene (CYR). To the best of our knowledge, experimental data in the literature for liquid-vapor equilibria or volumetric properties are relatively scarce in the operating conditions of pressure and temperature. For example, no experimental VLE data were found for the {CO₂ + CYR} system, and only low pressure and temperature or very high-pressure data are available for {CO₂ + GVL} pair.

First this work introduces the calorimetric and density measurement techniques developed in the lab and used to measure the experimental data. Then, new experimental enthalpies of solution and solubilities of CO₂ in the four BBSs (PC, ANI, GVL and CYR) were determined.

As mentioned before, the knowledge of mixture densities at different compositions, temperature and pressure conditions are important to optimize the process performance. But also, the densities of the pure solvents are crucial to calculate the molar flow rate of the BBS and thus the mixture composition. For this reason, densities of pure cyrene and anisole are also presented. Finally, all the experimental data were used to compare the solubility of CO₂ in the BBSs and to compare them with experimental or modeling data found in the literature.

After carefully reviewing the existing thermophysical data for bio-based solvents with carbonyl, ether, or ester functions and using molecular simulations to predict missing ones for pure BBS and CO₂+BBS mixtures, we have selected about 20 solvents including propylene carbonate, anisole, γ -valerolactone, and cyrene. All systems ({CO₂ + PC}, {CO₂ + ANI}, {CO₂ + GVL} and {CO₂ + CYR}) have not or not enough experimental enthalpic and volumetric data available in the literature for the needed temperature and pressure conditions (Fig. 1). For that purpose, new experimental VLE and enthalpy of solution data were determined for these systems at 333.15 K under a pressure of 4.00 MPa using a flow calorimetric technic. Densities of pure cyrene and anisole were also measured at 298.15 K and sup-ambient pressures using Anton Paar HPM vibrating-tube densimeter.

2.1. Materials

All chemicals needed for this work, their suppliers and purities are presented in Table 1. They were all used without further purification.

Table 1. Chemicals used in this work, suppliers, and mass fraction purity

Chemical	Supplier	Purity ^a
Cyrene	Merck	> 99 %
Propylene Carbonate	Sigma-Aldrich	99 %
Anisole	Sigma-Aldrich	99 %
γ -valerolactone	Sigma-Aldrich	≥ 99.9 %

^a As informed by the suppliers.

2.2. Enthalpic measurements

The purpose of this work is to measure the thermal effect occurring during CO₂ mixing with BBS and thus the mixing enthalpy of CO₂ in the BBS. The experimental technique used has already been detailed by Arcis et al. (Arcis et al., 2011) and is explained in the next paragraph.

2.2.1. Flow Calorimetric technique

The experimental arrangement is shown in Fig. 2.

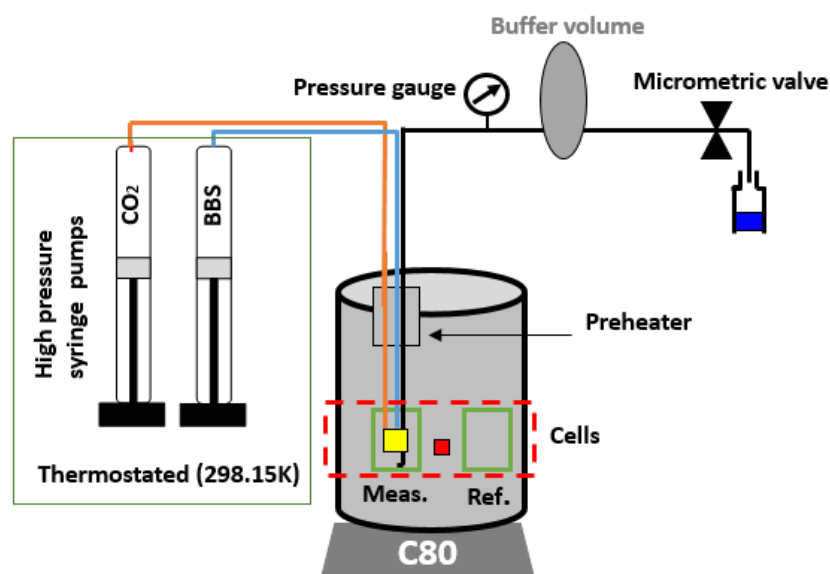


Figure 2. Schematic representation of the calorimetric technique

Measurements were performed using a custom-made ICCF-TIM flow mixing cell (Koschel et al., 2006) adapted to Calvet-type calorimeters C80. It is a heat exchange differential calorimeter manufactured by SETARAM allowing to work on a wide range of temperature.

The temperature of the block is adjusted by a G11 SETARAM controller and measured by a 200 Ω platinum (Pt) temperature sensor with an accuracy of 0.01 K; it is kept constant at ± 0.05 K during the whole experiment. In the center of the calorimeter block there are two identical wells that can hold two calorimeter cells; one used for measurement and the other for reference. In these wells there are thermopiles that measure the thermal power exchanged between the cells and the calorimeter bloc. Thermopiles are connected in a differential manner, thus eliminating the influence of any external interference.

As shown in Fig. 2, the two fluids are injected in the calorimeter mixing unit at constant volume flow rate using two high pressure syringe pumps (Isco Model 260 DM). These volume flows are converted to molar flows using the densities of the fluids. To ensure stable molar flow rates, the pumps are thermally controlled at 298.15 ± 0.1 K by a Fisher Scientific thermostat with water circulation. In order to adjust accurately the temperature of the entering fluids to the calorimetric bloc temperature, a pre-heater is inserted inside the calorimeter surrounding the fluids entering tubes. After being thermoregulated, the two fluids meet at the mixing point where the two concentric inlet tubes are connected to the mixing tube, at the bottom of the cell. Then the mixture flows into the mixture coiled tube which is in good thermal contact with the thermopiles allowing us to measure the heats of CO₂ dissolution in the BBS.

Finally, the mixture leaves the calorimeter via a buffer volume filled with nitrogen. The addition of this volume allows to limit the pressure fluctuations. The pressure is measured by an electronic Keller pressure gauge placed at the end of the line just before the buffer reservoir. For better control of the system pressure, a micrometric valve is added at the outlet of the unit allowing to decrease the system pressure by creating small leaks.

2.2.2. Operating procedure

Experiments were conducted at constant pressure (4 ± 0.005 MPa) and temperature (333.15 ± 0.03 K) and for different mixture compositions by changing flow rate ratio of the high-pressure pumps. With only absorbent circulating through the system, a stabilized baseline S_{BL} (mV) is recorded for approximately 20 minutes. Carbon dioxide is then injected into the circuit. Upon mixing with the absorbent, a thermal effect is detected by the thermopiles S_M (mV). This signal stabilizes and forms a "plateau" which is also recorded for about 20 minutes. The height of mixing signal from the base line is used to calculate the enthalpy of solution $\Delta_{sol}H$ following Eq.1.

$$\Delta_{sol}H/\text{kJ} \cdot \text{mol}^{-1} = \frac{(S_M - S_{BL})}{K \cdot \dot{n}_i} \quad \text{Eq. (1)}$$

where subscript i is for CO_2 or the BBS (PC, ANI, GVL or CYR), and K ($\text{mV} \cdot \text{mW}^{-1}$) is a calibration constant used to convert the thermopile signal (mV) to heat flux (mW). It may be determined from the Joule effect based on the heat delivered by a calibration heater or via a chemical calibration with two fluids where mixing enthalpy H_{mix} is known. The second method was employed in this work with the reference system {ethanol + water}, using enthalpy data provided by Ott et al. (Ott et al., 1986).

The molar enthalpy of solution of CO_2 in the BBS is determined as a function of gas loading charge α ($\text{mol} \text{CO}_2 \text{mol}^{-1}$ BBS) values until saturation of absorbent solution. It is calculated using the molar flow rates \dot{n}_i ($\text{mol} \text{s}^{-1}$) of the gas ($\Delta_{sol}H/\text{kJ} \text{mol}^{-1}$ of CO_2 , Fig. 4.a) or the molar flow rate of absorbent ($\Delta_{sol}H/\text{kJ} \text{mol}^{-1}$ of BBS, Fig. 4.b). The relative uncertainties on loading charge and enthalpies of solution are respectively less than 1.5% and 5% (Arcis et al., 2011).

The plots of enthalpy of solution $\Delta_{sol}H$ ($\text{kJ} \text{mol}^{-1}$ of BBS) were used to determine the gas solubility in the absorbent.

2.3. Density measurements

Knowledge of the molar flow rates \dot{n}_{CO_2} and \dot{n}_{BBS} is necessary to calculate the composition of the mixture and the enthalpy of solution accurately. Therefore, the densities of the studied fluids (CO_2 and solvents) must be known at the pump control temperature (298.15 K) and the pressure of the experiment (4 MPa). For CO_2 , we use the density presented by the National Institute of Standards and Technology (NIST) which is calculated using Refprop program. The densities of the different biobased solvents were measured at 298.15 K and as a function of pressure using a vibrating tube densimeter in static mode. the technique used is detailed as follows.

1.1.1. Vibrating-tube densimeter technique

The liquid density of the pure solvents was measured using Anton Paar HPM vibrating tube densimeter. In our application, the device was set up as shown in Fig. 3 to carry on measurements at 298.15 K and up to 9 MPa. It should be mentioned that density of pure BBS at high pressures are scarce in literature, for example we have not found any density data for anisole.

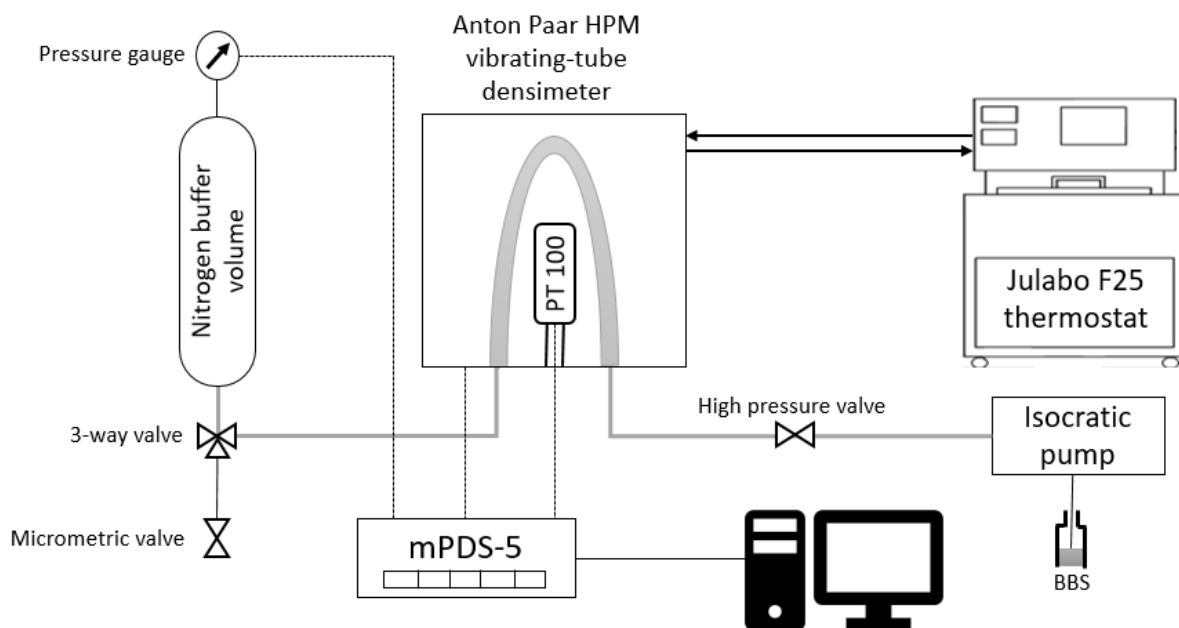


Figure 3. Schematic representation of the vibrating-tube technique.

The vibrating tube densimeter was connected to the mPDS-5 evaluation unit, which translates the electronic signal induced by the vibrating tube into the vibration period τ (μs). This interface is connected to a computer where the acquisition of the tube vibration period, temperature and pressure is performed using the HP VEE program.

To inject the solvent into the densimeter we use a KNAUER isocratic pump (AZURA P4.1S). The temperature of the vibrating tube is controlled using a circulator bath (Julabo model F25). It is measured directly inside the cell block and kept constant with a stability of 0.01 K. To pressurize the system, we use an auxiliary cylinder located at the outlet of the vibrating tube and filled with nitrogen at the required pressure. The fluid pressure is measured with a LEX1 digital manometer and kept constant during the time of the measurement.

1.1.2. Operating procedure

Before every sample loading, the densimeter and all tubes were washed with a volatile liquid (acetone) to make sure that any residue from previous measurements was removed. Next, nitrogen gas was circulated through the entire system to dry it of the washing liquid. Following this cleaning process, enough solvent volume to fill the vibrating tube was injected into the densimeter.

After reaching thermal equilibrium, the cell's vibration period was determined at different pressures, beginning with 2 MPa and then increasing to higher pressures, up to 9 MPa.

To begin the BBS density measurements, the densimeter was calibrated with vacuum and water (Wagner & Prub, 2002). This calibration was then validated with pure acetone in the temperature range of 288.15 to 328.15 K and at elevated pressures up to 9 MPa. The deviations between the experimental and NIST values were less than 0.3%.

3.1. Experimental results

The enthalpies of solution of CO_2 in propylene carbonate, anisole, γ -valerolactone, or cyrene were investigated at 333.15 K and 4 MPa, for different gas-solvent flow rate ratios. The numerical results are plotted versus gas loading charge (α) in Fig. 4. Large exothermic effects were observed. These graphs allow to differentiate the sections before and after saturation of the absorbent by the carbon dioxide.

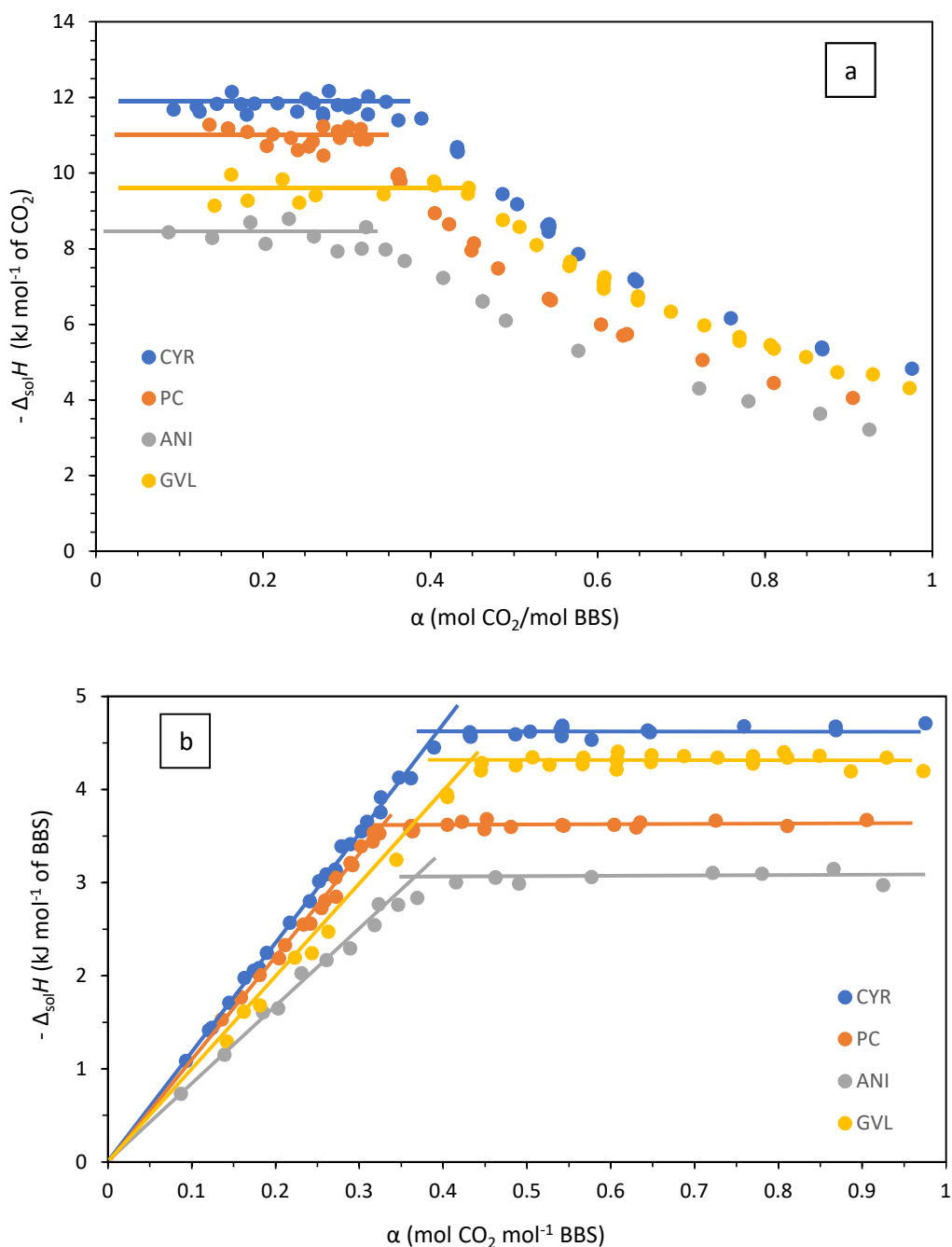


Figure 4. Enthalpy of solution ($-\Delta_{sol}H$) of CO₂ in the different BBSs (CYR, PC, ANI or GVL) versus CO₂ loading (α) at 333.15 K and 4.00 MPa. (a) $\Delta_{sol}H$ /(kJ mol⁻¹ of CO₂), straight lines show the average values for the enthalpies of solution at low loadings ($\alpha < 0.5$). (b) $\Delta_{sol}H$ /(kJ mol⁻¹ of BBS).

First, for the lowest loading charges ($0 < \alpha < 0.4$), we have an unsaturated solution, and the gas is fully absorbed by the solvent. In this domain, when the enthalpy of solution $\Delta_{sol}H$ is expressed per mole of CO₂ (Fig. 4.a) we observe a “plateau” and the average energetic value ($\Delta_{sol}H^{av}$) corresponds to the enthalpy of solution of CO₂ in the BBS at the experimental temperature and pressure conditions. While when it is expressed per mole of BBS (Fig. 4.b), $\Delta_{sol}H$ increases approximately linearly with the loading charge. The value of the slope corresponds to $\Delta_{sol}H^{av}$ obtained previously by the other graph.

The second domain represent a partial dissolution of CO₂ in the solvent, it is a saturated solution. This region is characterized by a decreasing exothermic effect with the loading charge when the enthalpy is per mole of CO₂ and a constant average value when it is per mole of BBS.

The intersection between these two domains, obtained graphically, corresponds to charge load used to calculate the solubility limit of the gas in the studied solvent given by carbon dioxide molar fraction (x_{CO_2}). The determination of this solubility limit is more obvious when the enthalpies of solution are expressed in mole of BBS. This method provides an indirect estimation of solubility with a 5% to 9% uncertainty. It depends on the accuracy with which the first point of the saturated domain is identified.

The densities of pure anisole and cyrene were measured at 298.15 K and constant pressures from 2 to 9 MPa. The numerical results are represented graphically in Fig. 5.

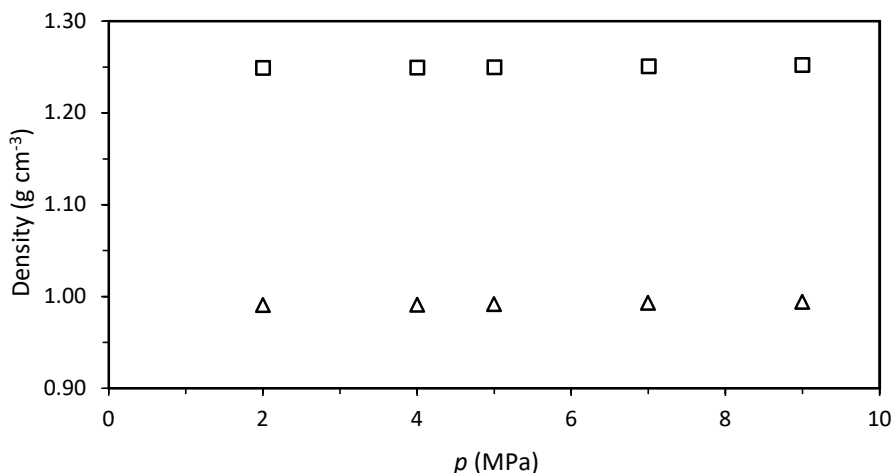


Figure 5. Densities of pure cyrene and anisole measured experimentally in this work at 298.15 K and sup-ambient pressures from 2 up to 9 MPa; Δ anisole; \square cyrene.

3.2. Discussion

The 333.15 K temperature and 4 MPa pressure were chosen to reproduce the conditions of the generator in a single-stage vapor absorption cycle. The enthalpy of solution $\Delta_{sol}H$ (kJ mol⁻¹ of dissolved CO₂) and the gas solubility were determined simultaneously from the plots in Fig. 4 as described above.

The obtained results showed on one hand that the enthalpies of solution for carbon dioxide in the studied solvents are exothermic under these temperature and pressure conditions. It should be reminded that the enthalpy of solution is the opposite of the minimum heat that must be provided to the mixture in order to separate the CO₂ from the solvent, this is especially important in the generator part of the absorption refrigeration machine. According to Fig. 4.a, at 333.15 K and 4 MPa, the desorption of CO₂ from cyrene requires the greatest amount of energy, followed by propylene carbonate and γ -valerolactone, and finally anisole with the lowest absolute value of enthalpy of solution. It should also be mentioned that this property $\Delta_{sol}H$ decreases in absolute value with increasing temperature. Indeed, the average absolute value $\Delta_{sol}H^{av}$ for cyrene at low loading charge (for $\alpha < 0.5$) and 313.15 K (Coulier et al., 2022) is higher than that at 333.15 K for the same pressure as shown in Fig. 6. No other experimental data were found in the literature for a direct enthalpies of solution comparison for the studied solvents under the pressure and temperature conditions of our present work.

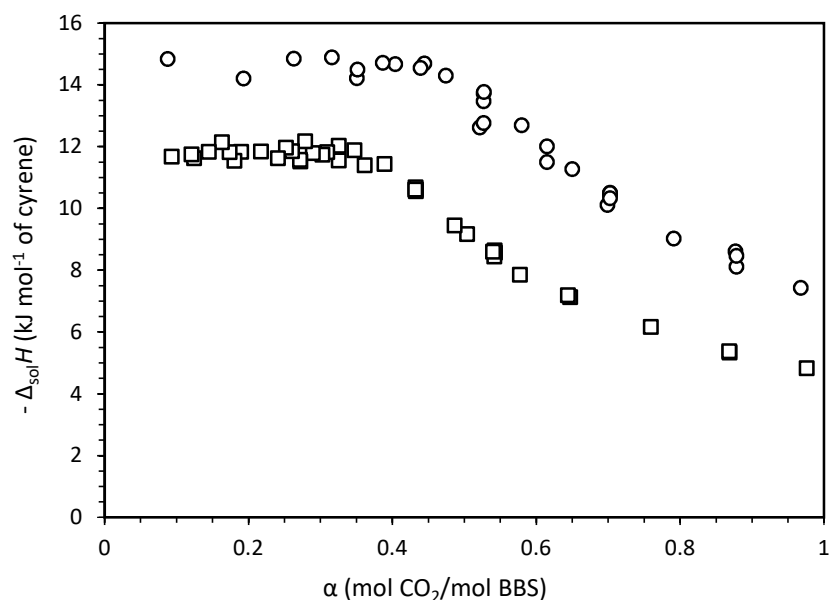


Figure 6. Enthalpy of solution of CO₂ in cyrene versus CO₂ loading (α) at 4.00 MPa and: □ 333.15 K (this work); ○ 313.15 K (Coulrier et al., 2022)

On the other hand, the solubilities of carbon dioxide at 333.15 K and 4 MPa in the different BBSs are almost the same with a slight variation in the following order PC < ANI < CYR < GVL.

Based on our previous experimental data [12], we note, in Fig. 7, that the CO₂ solubility in cyrene under the same pressure 4 MPa at 313.15 K is a bit higher than that at 333.15 K. This agrees with the results of enthalpy of solution showing an exothermic carbon dioxide dissolution in the solvents ($\Delta_{sol}H < 0$).

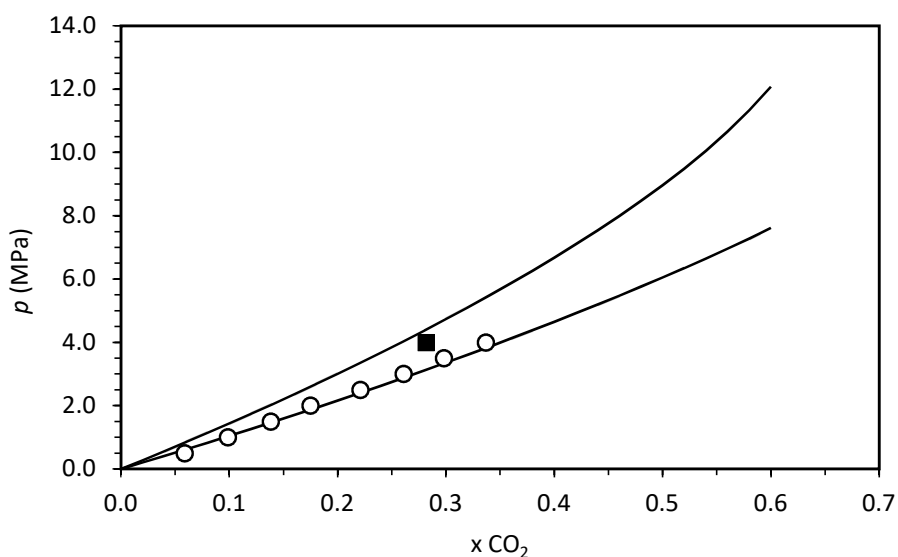


Figure 7. CO₂ solubility in cyrene at: ■ 333.15 K (this work); ○ 313.15 K (Coulrier et al., 2022); — SRK model ($k_{ij} = -0,01368$)

Unlike the CO₂ + CYR system for which no thermodynamic data can be found in the literature, the solubility of CO₂ in propylene carbonate has been studied for a wide temperature and pressure ranges using direct phase equilibrium measurements. To test the accuracy of the solubility determined by the calorimetric method in our work, we used the experimental data at 333.15 K from Williams et al. (Williams et al., 2002) and Hongling et al. (Hongling et al., 2011). We plotted, on the same graph the predicted values from a solubility correlation model. As demonstrated in Fig. 8, our results exhibit a great agreement with the literature values and the thermodynamic model used to correlate all the experimental data.

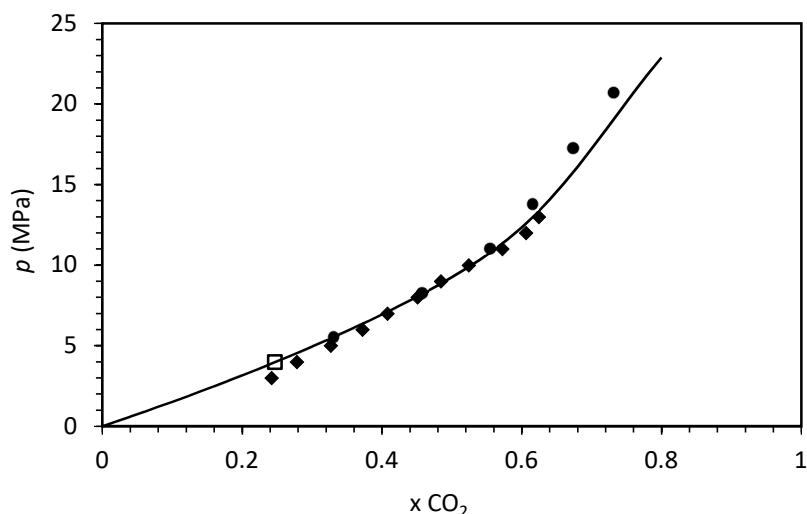


Figure 8. CO₂ solubility in propylene carbonate at 333.15 K: □ this work; ● (Williams et al., 2002); ◆ (Hongling et al., 2011) — SRK model ($k_{ij} = -0,010294$)

We also compared the experimental solubility of CO₂ in anisole with the calculated value obtained with the model presented in our last work (Coulier et al., 2022). The parameter for this model was determined by using the experimental vapor-liquid equilibrium data measured by Park et al. (Park et al., 1991). All the data used to describe the VLE for the system {CO₂ + ANI} at 333.15 K are reported in Fig. 9. This figure shows a very good consistency between our experimental results and those of the literature. Indeed, our measurement appears as a continuity of Park et al. measurements at lower pressure. A good agreement is also observed with the SRK model.

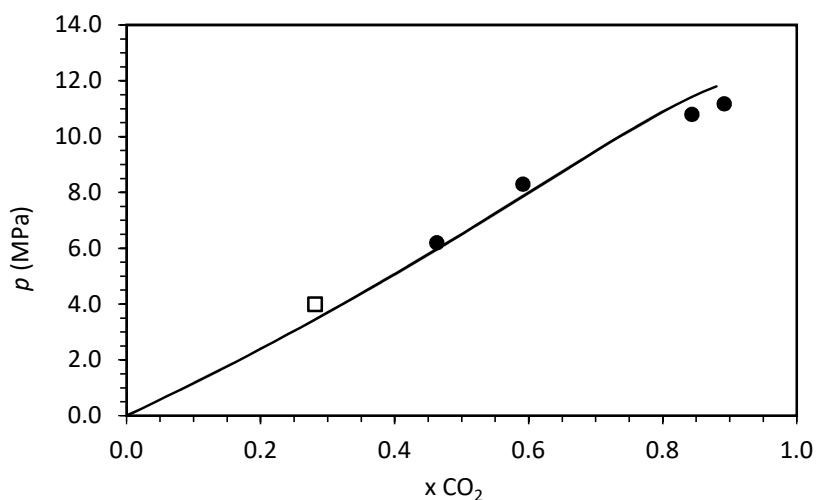


Figure 9. CO₂ solubility in anisole at: □ 333.15 K this work; ● 333.2 K (Park et al., 1991); — SRK model ($k_{ij} = 0.04084$)

For density results, as shown in Fig. 5, the cyrene is denser than the anisole at 298.15 K and for any given pressure. The results for both pure solvents show an almost unnoticeable increase in densities with pressure. This slight pressure dependence is more clearly illustrated by the experimental measurements of Baird et al. (Baird et al., 2019) for cyrene as presented in Fig. 10. However, no experimental data of anisole density was found in the literature.

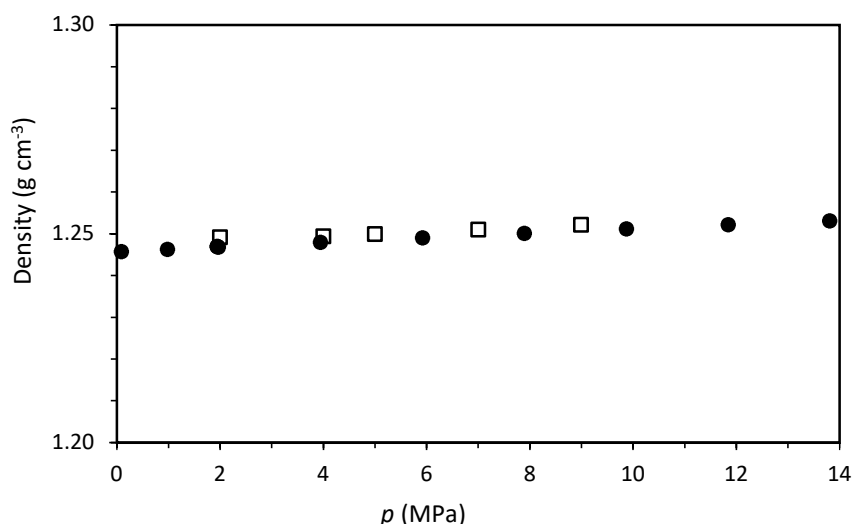


Figure 10. Densities of cyrene measured at constant temperature 298.15 K and sup-ambient pressures; □ this work; ● (Baird et al., 2019)

In this paper, new experimental data of thermodynamic and volumetric properties of $\{\text{CO}_2 + \text{BBS}\}$ systems have been presented. Four different solvents were studied: propylene carbonate, anisole, γ -valerolactone and cyrene. Densities of pure anisole and cyrene were determined at 298.15 K from 2 up to 9 MPa using a vibrating-tube densimeter. The enthalpy of solution and vapor-liquid equilibrium data were also measured at 333.15 K and 4 MPa using a flow calorimetric technique. The results showed on one hand that the CO_2 absorption into cyrene releases the largest amount of energy, followed by propylene carbonate, γ -valerolactone, and anisole. In the other hand, the solubilities of carbon dioxide in the different BBSs are almost the same with a slight variation in the following order $\text{PC} < \text{ANI} < \text{CYR} < \text{GVL}$. Finally, a comparison with existing literature data in section 3.2 showed the accuracy of our measurements.

The calorimetric technique allowed to determine with accuracy the solubility of CO_2 in the bio-based solvent at the desired conditions of temperature and pressure. However, this technique requires large amounts of solvent. Therefore, an original approach combining the flow calorimetric and a spectroscopic technique will be used in the future. In fact, IR spectroscopy will be used as a complementary technique to quickly measure numerous data point but with a lower precision. To complete this study, other selected bio-based solvents will be studied and other properties will be also measured such as density of $\{\text{CO}_2 + \text{BBS}\}$ mixtures, excess enthalpies and specific heat capacities (C_p). This work will be then an imperious prerequisite to benchmark potentially usable thermodynamic models and fit model parameters especially with the scarcity of experimental data in literature.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from the French projects ANR-20-CE05-0004 AWARE and PAI, supported by the French government and the Auvergne Rhone Alpes region.

NOMENCLATURE

K	Calorimeter calibration constant (mV mW^{-1})	k_{ij}	binary interaction parameter
\dot{n}_i	molar flow rate of the CO_2 or the absorbent (mol s^{-1})	p	pressure (MPa)
T	temperature (K)	x_{CO_2}	CO_2 molar fraction in liquid phase
$\Delta_{\text{sol}}H$	enthalpy of solution ($\text{kJ}\times\text{mol}^{-1}$)	α	CO_2 loading charge ($\text{mol CO}_2/\text{mol}$ absorbent)

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