

# Measurements of the High-Pressure Phase Equilibria for the System Carbon Dioxide – Limonene by Means of a Double-Chamber Recirculation Apparatus

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## ABSTRACT

Limonene is the major monoterpene compound of lemon essential oil, which is a valuable raw material for the food, cosmetics and perfume industry. This essential oil is mainly composed of monoterpenes (more than 90% of the oil), monoterpene oxygenated derivatives and sesquiterpenes. The removal of monoterpenes from lemon essential oil (deterpenation process) is a common industrial practice which allows increasing the concentration of the oxygenated compounds, which are the most valuable, and the stability of the oil. This process can be successfully performed by means of supercritical carbon dioxide. Information on high-pressure phase equilibria related to carbon dioxide and the main components of the essential oil is relevant for the supercritical deterpenation process design. In this work, measurements of the phase equilibria for the system carbon dioxide – limonene were performed at 70°C and in the pressure range 8.54 – 13.34 MPa. These data are of particular interest because these operating conditions are relevant for the supercritical deterpenation process [1] and literature data at 70°C are scarce. The experimental measurements were performed by means of a two-chamber apparatus. In the first chamber (“equilibrium cell”) the liquid phase coexists with the gas phase, whereas the second chamber (“gas cell”) contains only the gas phase, which is continuously recirculated through the chambers in order to reduce time for equilibration. Before sampling of the phases, the cells are separated by closing valves in order to avoid any disturbances of the equilibrium when the pressure is reduced during the withdrawal of the gas phase. In the experimental pressure range, the solubility of limonene in the gas phase increases from 12.3 to 86.4 g/kg, whereas that of carbon dioxide in the liquid phase increases from 0.34 to 1.17 g/g. The experimental results were compared to the data measured by means of the same procedure at 50°C [2]. Increasing temperature from 50 to 70°C, limonene solubility in the gas phase decreases moderately, whereas the solubility of carbon dioxide in the liquid phase decreases markedly.

## INTRODUCTION

Lemon essential oil is a valuable raw material for the food, cosmetics and perfume industry because of its flavour and fragrance. It is mainly composed of monoterpenes, which make up more than 90% of the oil, monoterpene oxygenated derivatives and sesquiterpenes. The major constituent of the monoterpenes, which are C<sub>10</sub> unsaturated hydrocarbons, is limonene (4-isopropenyl-1-methyl-1-cyclohexene), which makes up more than 50% of the essential oil. The removal of monoterpenes from lemon essential oil (deterpenation process) is a common industrial practice which allows increasing the concentration of the oxygenated compounds, which are the most valuable, and the stability of the oil. It was proved that the deterpenation process can be effectively performed through supercritical carbon dioxide [1, 3], which allows the essential oil to undergo minimal alteration mainly because of low operating temperature and complete removal of the solvent from the oil [3, 4].

Experimental data on high-pressure phase equilibria related to carbon dioxide and the main components of lemon essential oil are the basis of the supercritical deterpenation process design. In this regard, measurements on phase equilibria of the system carbon dioxide – limonene are of primary importance. This binary system has been extensively studied by various authors, which mainly focused on temperatures below 60°C [2, 5-18]. On the other hand, only a few data including higher temperatures are available [19-21].

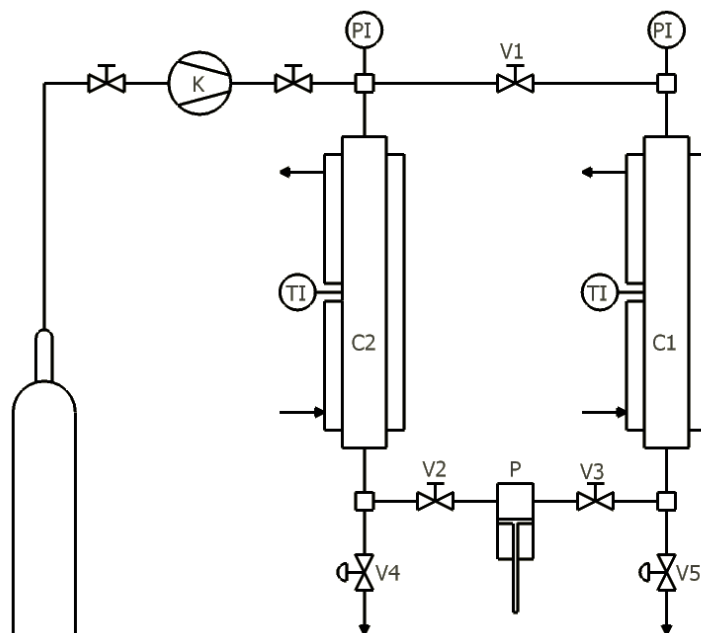
In spite of the scarcity of phase equilibrium data above 60°C, operating temperatures up to 85°C are reported in the literature for separation columns which perform deterpenation of citrus essential oils by means of supercritical carbon dioxide [3]. Furthermore a study on the supercritical deterpenation process, based both on experiments and process modelling, showed that performing the process at 70°C makes possible to identify operating conditions which are particularly favourable [1]. Therefore phase equilibrium data at 70°C have both theoretical and practical relevance.

This work deals with measurements of the high-pressure phase equilibria for the system carbon dioxide – limonene, which were performed at 70°C and performed in a pressure range of practical relevance for the deterpenation process (8.54 – 13.34 MPa). The apparatus and the procedure used in the present work were set up and validated in a previous work on this subject [2], where the phase equilibria of the same system were measured at 50°C and the experimental data were analysed in comparison to literature data. The proposed apparatus is composed of two chambers in order to allow the isolation of a large volume of gas phase at equilibrium and its sampling without disturbing the two-phase equilibrium established in the other chamber. The time necessary to reach the equilibrium is reduced by continuously recirculating the gas phase through the two chambers. Both the composition of the liquid and the gas phase at equilibrium are measured. The experimental data reported in the present work are discussed taking into account the available literature data at 70°C [19-21] and the data measured at 50°C by means of the same apparatus and procedure [2].

## APPARATUS AND MATERIALS

The apparatus used for the experimental measurements of high-pressure phase equilibria is shown in Fig. 1. It is composed of two chambers (C1 and C2), of 170 cm<sup>3</sup> each (i.d. 16 mm). The chambers are provided with heating jackets, which are connected to a thermostatic bath by means of two distinct lines. The top of each chamber is connected to a digital pressure gauge (DMM 250 bar, AEP Transducers, Italy), calibrated and certified by the Italian SIT. In the range of experimental pressures of the present work (8.54 – 13.34 MPa) the maximum uncertainty on pressure measurements at 70°C is ±0.05 MPa. The two chambers are also provided with two thermocouples, which allow to measure the temperature in each chamber with an uncertainty of ±0.1°C. The gas phase at the operating pressure can be recirculated between the two chambers by means of an air driven high-pressure piston pump (Haskel 4B-150, label P in Fig. 1), which displaces a small volume of fluid per cycle (1.44 cm<sup>3</sup>). The two chambers can be separated by means of the closing valves V1, at the top, V2 and V3, at the bottom. The valves V4 and V5 are high-pressure micrometer valves, which allow a fine flow rate regulation. The valves V4 and V5 are employed to sample the gas and the liquid phase, respectively. A membrane compressor (K) allows the two chambers to be fed with supercritical carbon dioxide, which enters the top of the chambers according to Fig.1.

As for the materials used in this work, carbon dioxide is 99.9% pure (Siad, Italy), whereas limonene has been purchased from Sigma-Aldrich [R-(+)-limonene, C<sub>10</sub>H<sub>16</sub>, molecular weight 136.24, code 183164, purity 97%].



**Figure 1:** Apparatus for high-pressure phase equilibrium measurements. C1: equilibrium cell. C2: gas cell. K: membrane compressor. P: high-pressure piston pump. V1, V2, V3: closing valves. V4, V5: high-pressure micrometer valves.

## EXPERIMENTAL METHODS

The experimental procedure used in this work was fixed through a number of preliminary runs and validation tests which are described in a previous work on this subject [2]. The fixed procedure was already applied to measure the phase equilibria of the system carbon dioxide – limonene at 50°C, in the pressure range 8.5 – 10.1 MPa [2]. The main steps of the experimental procedure are reported in the followings. At the beginning of each experimental run approximately 20 g of limonene are fed to the chamber C1 (the “equilibrium cell”). The heating circuit is switched on and carbon dioxide is fed by the membrane compressor to both chambers, until the desired pressure is reached. As a result, the liquid and the supercritical fluid are contacted in the equilibrium cell, whereas in the chamber C2 (the “gas cell”) pure carbon dioxide is contained at the initial time. Subsequently the closing valves V2 and V3 are opened and the recirculation pump is switched on. Thus, the gas phase is continuously recirculated from the cell C2 to the cell C1, in order to reduce time for reaching the equilibrium condition. The high ratio of the volume of each chamber to the volume displaced by the pump (P) in a cycle, which is around 118, guarantees a small pressure oscillation in the two chambers during the recirculation. The pressure oscillation induced by the pump on the system, observed in the experimental runs, never exceeded 0.04 MPa. The pump operates at 60 cycles per minute for a 6 hour duration. These values correspond to an overall recirculated volume greater than 180 times the volume of each chamber. During the recirculation period, a small amount of fresh carbon dioxide is sporadically fed to the system in order to maintain the pressure at the desired value. The pressure reduction to be balanced is caused by carbon dioxide solubilisation in the liquid phase. In fact, this pressure reduction is more noticeable at the beginning of the recirculation period, whereas it tends to zero when the system is approaching equilibrium. After approximately 4 hours from the initial time, the pressure of the system is stable without feeding further carbon dioxide.

At the end of the recirculation period, the valves V1, V2 and V3 are closed, in order to separate the two cells. In this way, it is possible to sample the gas phase contained in the gas cell, without disturbing the two phase system in the equilibrium cell. Furthermore, the

double-chamber system allows sampling the whole content of the gas cell, which is of 170 cm<sup>3</sup>. Thus, it is possible to get a large amount of the gas phase and, as a consequence, a sufficient amount of solute for the analysis. This is noteworthy for systems of interest in supercritical processing because the liquid solubility in supercritical carbon dioxide is typically low.

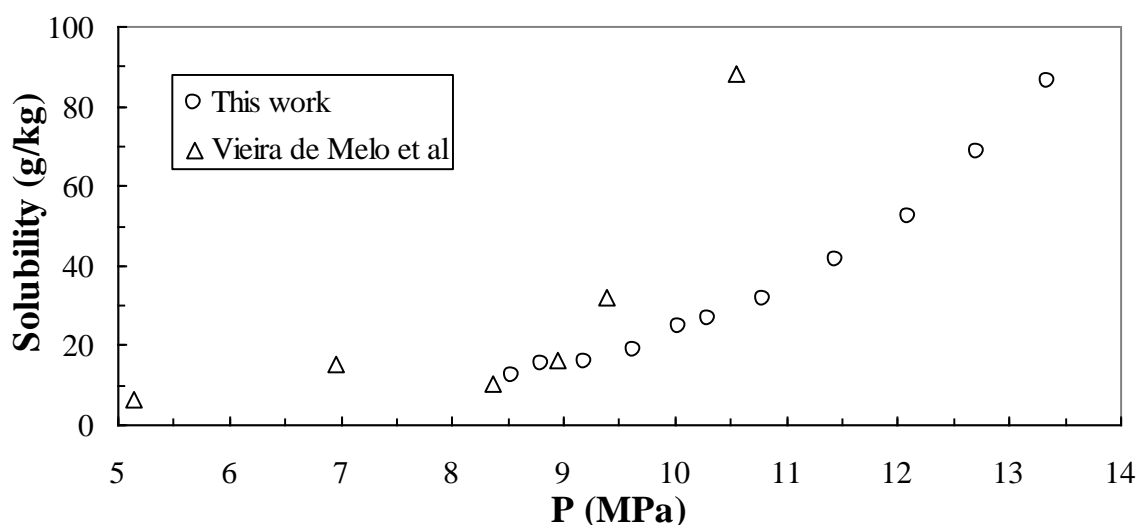
The sampling of the gas phase begins with the pressure reduction of the gas cell down to the atmospheric value, by tuning the opening of the valve V4. During this operation, the content of the gas cell is conveyed to a sampling flask that is maintained at atmospheric pressure and immersed in a thermostatic bath at about -25°C, in order to minimize limonene losses caused by evaporation. Because of decompression, the solute exiting the valve V4 condenses and can be collected in the cold sampling flask. The amount of solute recovered (in the range 0.6 – 6.7 g in the equilibrium measurements of the present work) is determined gravimetrically, whereas the volume of the gas exiting the sampling flask is measured in a gas flow meter (S.I.M. Brunt AB1; minimum flow rate 1 l/h; nominal flow rate 460 l/h; Italy). In order to determine the total amount of carbon dioxide in the cell C2 at equilibrium, the moles of carbon dioxide that flow through the flow meter are added to the moles that remain in the cell at the end of the depressurization (atmospheric pressure, equilibrium temperature), which are calculated by means of the ideal gas equation of state. After the decompression step, the gas cell is pressurized again and then it is washed by continuously flowing supercritical carbon dioxide. The amount of carbon dioxide that flows in the washing step is set equal to the amount that exits the cell in the depressurization step. The gas flow rate is maintained at 1 l/min (measured at ambient temperature and atmospheric pressure) both in the depressurization and in the washing step. The solute collected in the washing step is, on average, 25% of the total solute recovered, that is to say that the simple decompression would result in incomplete sampling. This is likely to be caused by the drastic lowering of the liquid solubility in carbon dioxide when reducing the pressure of the cell that causes the solute to re-condense inside the chamber. As a consequence, part of the solute is likely to remain on the walls of the chamber and can not be collected in the decompression step. It was estimated that the solute recovery by the two-step sampling procedure (decompression – washing) is, on average, 99.4% [2].

Liquid sampling is performed after completing the gas sampling procedure, which typically lasts for about 90 minutes. During this period the equilibrium cell C1 is maintained closed, at the equilibrium temperature and pressure and it is unaffected by the gas sampling. A small amount of the liquid phase is withdrawn by opening slowly the valve V5 and conveying the sample to a flask at atmospheric pressure. The liquid is collected in the flask and its amount is determined gravimetrically, whereas carbon dioxide is conveyed to the gas flow meter. The sampling procedure lasts until 1 litre of carbon dioxide is measured (at atmospheric pressure and ambient temperature). This value was selected in order to take into account two contrasting factors: a large sampled volume provides a sufficient amount of collected liquid to be weighted accurately but, at the same time, it results in a pressure lowering of the chamber that can alter the equilibrium composition. Sampling the above-mentioned volume of carbon dioxide in the equilibrium experiments resulted in a liquid withdrawal in the range 1.5 – 5.5 g. The pressure drop in the equilibrium cell caused by the liquid sampling varies from approximately 0.25 MPa (2.9% of the total pressure) at the lowest pressure values, to 0.17 MPa (1.3% of the total pressure) at the highest pressure values. Values of pressure drop during sampling of about 2% of the total pressure are generally considered reasonable [23].

## RESULTS AND DISCUSSION

The experimental measurements on the binary system carbon dioxide – limonene were performed at 70°C, in the range of pressure 8.54 – 13.34 MPa. The composition of both the gas and the liquid phase was measured for 11 pressure values. The experimental data measured at 50°C by means of the same apparatus and procedure, reported in a previous work [2], are also taken into account for the present discussion. Despite the binary system carbon dioxide – limonene was extensively studied by several authors, only a few data are available at 70°C [19-21]. Vieira de Melo et al. [19] measured the equilibrium composition of both the gas and the liquid phase at 50, 60 and 70°C. At 70°C the authors measured the equilibrium compositions for 6 pressure values, in the range 5.14 – 10.55 MPa. Corazza et al. [21] measured bubble point pressures in the range 40 – 70°C. Unfortunately the authors do not report the experimental results at 70°C, but they just state that the deviations from the data reported by Vieira de Melo et al. [19] are always lower than 0.3 MPa. From a plot reported in another work by Corazza et al. [20], which is mainly focused on ternary systems composed of carbon dioxide, limonene and organic solvents, it can be deduced that the solubility of carbon dioxide in the liquid phase at 343 K and a pressure between 13.0 and 13.5 MPa is around 4.08 grams of carbon dioxide per gram of limonene. No other data at this temperature are reported or can be deduced.

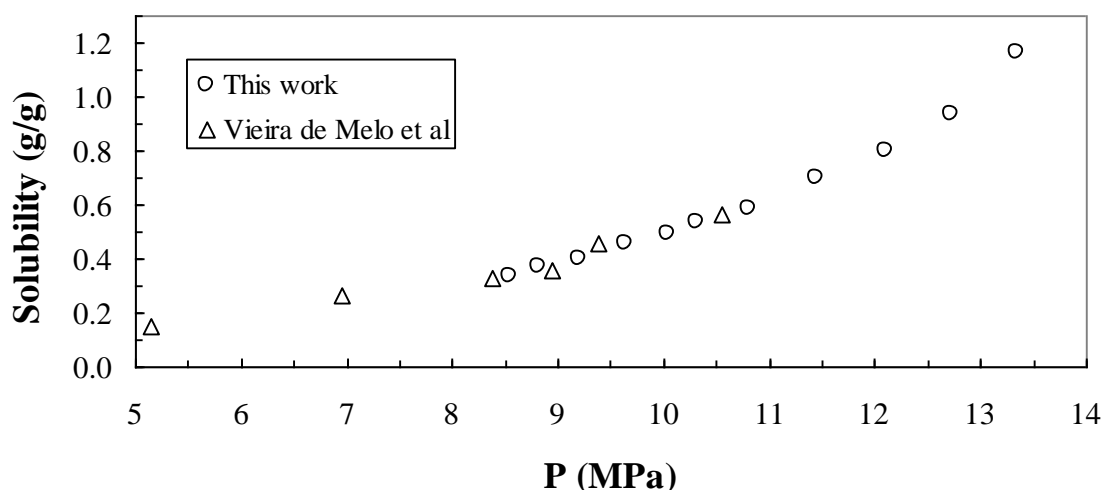
Fig. 2 reports the solubility of limonene in the gas phase as a function of pressure. Except the values at 10.80, 11.44, 12.10 and 13.34 MPa, each of the other 7 values represents the average of two replication of the same experiment. The average relative deviation (ARD) of the replicated runs is equal to 8.4% (with respect to the average solubility value, expressed as grams of limonene per kilogram of carbon dioxide). As expected, in the range of pressure under investigation the solubility of limonene in supercritical carbon dioxide increases with pressure and the slope of the solubility curve increases as well. The measured values rise from 12.3 g/kg at 8.54 MPa up to 86.4 g/kg at 13.34 MPa. The only possible comparison with literature data is that with the experimental data of Vieira de Melo et al. [19]. As it can be seen, data agree well between 8 and 9 MPa. On the other hand, large discrepancies are found above 9 MPa. In particular, the increase of solubility found in this work for pressures above 9 MPa is not so sharp as that found by Vieira de Melo et al. [19].



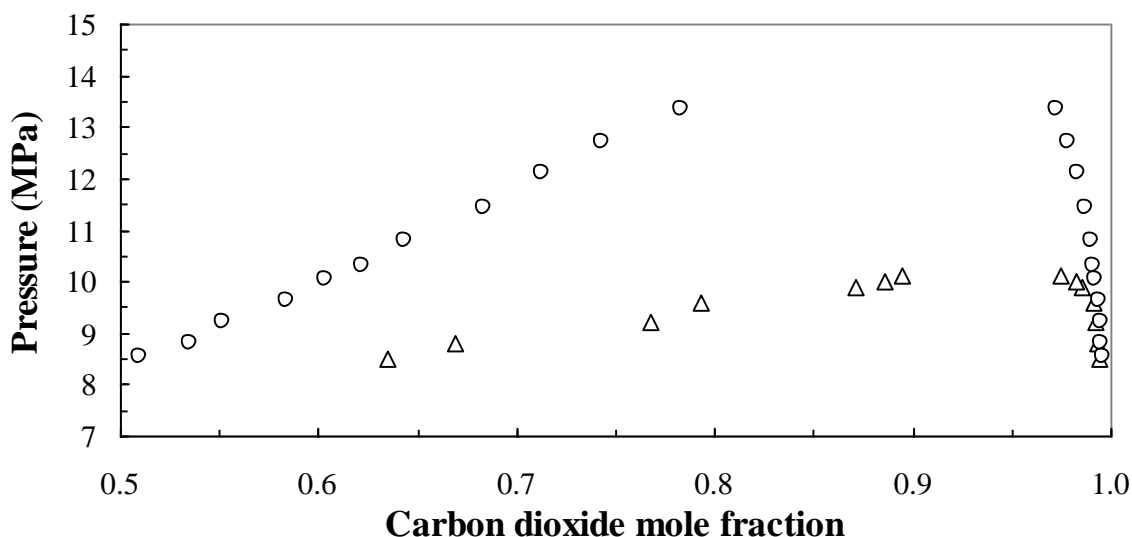
**Figure 2:** solubility of limonene in the gas phase at 70°C, as a function of pressure. Binary system: carbon dioxide + limonene. The solubility is expressed as grams of limonene per kilogram of carbon dioxide.

However, analysing the whole set of data reported by Vieira de Melo et al. [19], which refer to three temperatures (50, 60 and 70°C), it seems that the behaviour of solubility above 9 MPa is somewhat inconsistent. In fact, at 50°C the authors found 27.2 g/kg at 9.68 MPa (which is in good agreement with data reported in [2]), whereas they found 20.9 g/kg at 9.78 MPa; at 60°C a solubility of 19.0 g/kg at 10.07 MPa is reported; at 70°C the authors report a solubility of 31.9 g/kg and 88.2 g/kg at 9.39 MPa and 10.55 MPa, respectively. According to these data the solubility of limonene in supercritical carbon dioxide at constant pressure is expected to decrease between 50 and 60°C, whereas it is expected to increase sharply when temperature increases from 60 and 70°C. Furthermore, the data found in the present work are reasonably consistent with the experimental data on the deterpenation of lemon essential oil by means of supercritical carbon dioxide, which was performed in a continuous countercurrent column by Gironi and Maschietti [1]. In those experiments the vapour phase loading in the column at 70°C was about 20 and 26 g/kg at 10.3 and 11.2 MPa, respectively. Since the solubility of lemon essential oil is approximately equal to that of limonene (see for example [2]), these data are inconsistent with a solubility of limonene as high as 88.2 g/kg at 70°C and 10.55 MPa, as reported by Vieira de Melo et al. [19].

As for the liquid phase, Fig. 3 shows the solubility of carbon dioxide as a function of pressure. With reference to the 7 experimental runs which were replicated twice, ARD on solubility in the liquid phase resulted to be equal to 4.3% (with respect to the average solubility value, expressed as grams of carbon dioxide per gram of limonene). As typical, the solubility of the gas component in the liquid phase increases as pressure increases. The solubility values range approximately from 0.34 g/g at 8.54 MPa up to 1.17 g/g at 13.34 MPa. As it can be seen, the agreement with the data of Vieira de Melo et al. [19], in the case of the liquid phase, is excellent. On the other hand, a solubility as high as 4.08 grams of carbon dioxide per gram of limonene at pressure between 13 and 13.5 MPa, as reported in a plot by Corazza et al. [20], is not found. Since the numerical value of the single experimental data measured by Corazza et al. [20] is not provided, this experimental point is not reported in Fig. 3. Finally the data at 70°C measured in this work are represented as bubble and dew point pressures in Fig. 4, together with the data referred to 50°C which were measured by



**Figure 3:** solubility of carbon dioxide in the liquid phase at 70°C, as a function of pressure. Binary system: carbon dioxide + limonene. The solubility is expressed as grams of carbon dioxide per gram of limonene.



**Figure 4:** bubble and dew point pressure for the system carbon dioxide – limonene at 50 and 70°C. Binary system: carbon dioxide + limonene. The solubility is expressed as grams of carbon dioxide per gram of limonene.

means of the same apparatus and procedure and reported in a previous work on this subject [2]. The analysis of the data at the two different temperatures shows that, for a given pressure below 9.6 MPa, the solubility of limonene in the gas phase at 70°C is approximately 30% less than the solubility at 50°C. Above 9.6 MPa, at 50°C, the system approaches the critical point of the mixture and the solubility of limonene in the gas phase increases sharply. At 10.1 MPa the mole fraction of carbon dioxide is 0.8942 in the liquid phase and 0.9750 in the gas phase. On the other hand, at 70°C and 13.34 MPa the two phases at equilibrium are still fairly distinct. In these conditions, the mole fraction of carbon dioxide is 0.7830 in the liquid phase and 0.9728 in the gas phase. In the range of pressure 8.5 – 10.1 MPa, as it can be seen from Fig. 4, the solubility of carbon dioxide in the liquid phase at 70°C is always lower than the solubility at 50°C. On average, for a given pressure the solubility at the higher temperature is 55% less than the solubility at the lower temperature. More specifically, at the lowest pressure under consideration the solubility at 70°C is around 40% less than the solubility at 50°C, whereas around 10 MPa the solubility at 70°C is approximately the 80% less than the corresponding value at 50°C.

## CONCLUSIONS

The phase equilibria of the system carbon dioxide – limonene at 70°C were determined in a range of pressure that has practical relevance for the supercritical deterpenation process (8.54 - 13.34 MPa). The reported data are original, since previously published data on this system at 70°C are very scarce and measured by different experimental procedures. A single publication reporting numerical data at 70°C, for pressures up to 10.55 MPa, was found in the literature [19].

The experimental data on the liquid phase reported in this work compare well to the data reported in [19]. As for the gas phase, data of the present work compare well up to 9 MPa, whereas large discrepancies are found at higher pressures. The data found in the present work were also analysed together with those previously measured at 50°C by means of the same apparatus and procedure [2]. The bubble point and dew point pressure curves at the two temperatures show a coherent behaviour.

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