

An apparatus for the investigation of the solubility of n-octadecane in supercritical carbon dioxide at 310, 313, 333 and 353 K, in the range 10 - 20 MPa.

Rafael Eustaquio-Rincón and Arturo Trejo*

Instituto Mexicano del Petróleo, Area de Investigación en Termofísica, Programa de Simulación Molecular, Eje Central Lázaro Cárdenas 152, 07730, México, D.F. (México)

e-mail: atrejo@imp.mx

Abstract

The optimization of temperature and pressure conditions for the extraction of n-octadecane with supercritical CO₂ have been investigated. This work presents experimental phase equilibria results of the study carried out at supercritical conditions for the system CO₂ + n-octadecane in the temperature range 310 to 353 K, and in the pressure range 10 to 20 MPa. The experimental work was carried out in a semi flow-type apparatus constructed in our laboratory, the amount of the extracted solute was determined gravimetrically. The equipment and experimental procedure were tested by performing measurements of the solubility of n-decane in supercritical CO₂ at 344.15 K. The solubility of n-octadecane in supercritical CO₂ increases as the pressure increases but the functionality with temperature shows a maximum solubility value at 313 K. The system pressure was measured to ± 2 kPa, temperature was measured to ± 0.05 K and the composition was determined to ± 0.00005 in mole fraction.

Keywords: Supercritical extraction, solubility, CO₂, n-octadecane.

Introduction

The supercritical phase is not a recent discovery. It has been recognized since the 19th century. However, during the last two decades the supercritical extraction has been widely exploited in industry, mainly due to its many advantages and because it is an environmentally friendly technology. Furthermore supercritical extraction technologies give products with greater purity than those obtained with the methods and solvents used nowadays. Using supercritical fluid extraction (SFE) is possible to extract high boiling and/or thermally sensitive materials, too. The advantage of supercritical extraction is, among others, its selectivity to dissolve different substances depending on the set pressure and temperature. Solvent recovery is not necessary, because the extracts are separated completely from the solvent by only decreasing the pressure.

A lot of solvents can be used in supercritical extraction processes like CO₂, methane, ethane, propane, n-hexane, propylene, water, etc. SFE is a technology with high potential of applications: Extraction of natural products like flavors, fragrances and preservatives; oil removal from tar sands; deasphalting of heavy oils, recovery of alcohol from aqueous solutions, etc. In particular supercritical CO₂ has been shown to be an excellent solvent. It has been used by the food industry since the late 70s, and recently it was used to extract carotenoids and lipids from a fruit and black pepper from essential oil (Ferreira et al., 1999a; 1999b). Then, the use of CO₂ allows to substitute harmful substances that are carcinogenic, explosive, environmentally harmful, etc. CO₂ possesses low critical point, it is easy and safe to handle, it is non toxic, non corrosive, non inflammable, stable at supercritical conditions, and has low price.

The field of application of industrial extraction at supercritical conditions is so important and realistic that there are a lot of companies that offer their technology for any client willing to develop his markets and introduce new products adapted to regulating laws, for example, Hitex (Mengal, 2000); Flavex (Flavex, 2000); Phasex (Krukoniš, 2000); Applied Separations, Inc.(King, 2000); Supramics[®] (Jones, 2000); Eco Waste Technologies (Boyd, 2000); Marc Sims SFE (Sims, 2000); etc.

In this work we have studied the solubility of n-octadecane in supercritical CO₂. The study was carried out in the temperature range 310 to 353 K, and in the pressure range 10 to 20 MPa using a semi flow-type apparatus.

Experimental

Materials

Carbon dioxide supercritical fluid extraction grade was provided by Praxair with a purity of 99.998 mol %, supplied with 2000 psig helium headspace pressure and with an eductor tube. N-decane and n-octadecane were obtained from Merck synthesis grade, with a purity of 99 mol % and 98 mol %, respectively. N-hexadecane was obtained from Aldrich, with a purity of 99+ mol %. All the samples were used without further purification.

Apparatus

Phase behavior measurements at subcritical and supercritical conditions have been made in different types of apparatuses, in particular, flow type apparatuses have been used extensively for studying lots of very different systems. For example, Kurnik and Reid in 1982 studied the solubilities of binary, solid hydrocarbon mixtures in both supercritical

carbon dioxide and supercritical ethylene at 308 and 318 K in the pressure range 12 to 28 MPa. Finn and coworkers in 1983 studied the extraction of coal with supercritical hydrocarbon mixtures in the temperature range 693 to 753 K and in the pressure range 5 to 20 MPa. Inomata and coworkers in 1986 measured the vapor-liquid equilibria of n-heptane, n-decane, transdecalin, tetralin, and quinoline with supercritical CO₂, in the temperature range 340 to 710 K at several pressures up to 25 MPa. Recently Choi and coworkers (1998) studied the solubilities of isomeric o-, m-, and p-coumaric acid isomers in high-pressure carbon dioxide at 308 -323 K and 8.5 - 25 MPa. All of them reported several advantages observed when using a flow type apparatus. For example, the vapor and liquid phase concentrations were independent of the flow rate of CO₂ employed; the apparatus is adaptable to a wide variety of feedstocks; it is possible to reduce the residence time of heat sensitive substances at high temperatures; equilibrium, stripping, or fractionation data can be obtained; etc.

However, the disadvantages of this type of flow systems must be considered: A heavy solid or liquid can clog the metering valve; undetected phase changes can occur in the presaturator or equilibrium cell; high pressures can cause the density of the SCF-rich phase to become greater than the density of the solute-rich liquid phase, which results in the SCF-rich phase pushing the liquid phase out of the equilibrium cell thus leading to erroneous solubility information; etc.

A semi-flow type apparatus was designed and constructed in this study in 316 stainless steel. This apparatus can be operated from ambient to 423 K and up to 20 MPa. The main components of the apparatus are feeding, equilibrium and sampling sections. Figure 1 shows the apparatus.

Feeding section. CO₂ from the commercial cylinder is introduced into a 4 liter thermocompressor. The thermocompressor is heated with an electrical resistance in order to increase the CO₂ pressure. The CO₂ is then passed into a feeding cell, which is immersed in a constant temperature water bath. The feeding cell pressure is maintained at least 0.1 MPa above the equilibrium pressure and during the experiment this pressure gradient is maintained by means of increasing the temperature of the bath in which the feeding cell is thermostated. The pressure gradient is useful to inject CO₂ with a fine control into the equilibrium section.

Equilibrium section. There are two cells in this section; one serves as pre-saturator and the other one is properly the equilibrium cell, both are immersed in a Tamson bath model TV4000, with a temperature control within ± 0.02 K in the range of temperature studied. The temperature is measured to ± 0.01 K with a platinum resistance thermometer from Automatic System Laboratory, model F250, calibrated with an AC Bridge, traceable to the NIST. The Pressure is measured with a differential pressure transducer Validyne, model DP15, calibrated in the range 0 - 20 MPa, with a deadweight balance from Pressurements, model T2200/3LP with an accuracy of ± 0.03 % in the full range.

Once the temperature and pressure are controlled in the feeding section the CO₂ is allowed to flow from this section through the pre-saturator cell. There is a tubing section of 6 meter long between the feeding section and the pre-saturator in order to preheat the CO₂. Then the CO₂ is introduced into the equilibrium cell and sent to the sampling system.

Sampling section. The effluent from the equilibrium cell is withdrawn through a micrometering valve, flashed into a Pyrex cell, where the liquid solute is collected and the

CO₂ flows through a wet test meter from Precision Scientific Inc, model 63126, with precision of ± 0.01 liter. The liquid condensed in the cell is weighed in an Ohaus balance, model GT410, with resolution of ± 0.001 g.

Methodology

At the beginning of the experiment, the pre-saturator and equilibrium cell are charged with 80 and 50 g, respectively, of the solute. Then, the thermocompressor, feeding cell, pre-saturator and equilibrium cell are fed with CO₂ at the same pressure than the CO₂ commercial cylinder. Next, all the metering valves are closed and the thermocompressor is heated in order to increase its pressure and immediately CO₂ is passed through the feeding cell. The metering valve located between the feeding and equilibrium sections is opened and the flow of CO₂ is regulated with it. The pressure in the equilibrium section is maintained by adjusting the opening of the metering valve mentioned above. The solute sampling is started after one hour approximately, once the steady state was attained.

Each solute sample is collected during the necessary time to flow 15 liters of CO₂ through the equilibrium cell, the condensed phase must be stored at a temperature above the solute melting point in order to avoid occlusions of the system. The amount of extracted solute is determined with an analytical balance. The results reported in this work are the average of 3 measurements at isothermal and isobaric conditions.

Only minor corrections are made, the amount of extracted solute is corrected by the solute vaporized calculated from its vapor pressure and the temperature of the flask in the sampling section.

Results and discussion

The apparatus and experimental methodology were tested through the study of two binary systems, one of them was CO₂ + n-decane, at 344.15 K. We chose to study this system due to the fact that it has been studied by several authors (Reamer and Sage, 1963; Nagarajan and Robinson, 1986; Chou et al., 1990; and Jennings and Schucker, 1996), furthermore the available data are highly consistent.

Figure 2 shows that data from this work are in good agreement with all the data previously reported. The differences between our experimental data and those obtained by Reamer and Sage are given in figure 3, together with a comparison between the results reported by Nagarajan and Robinson, Chou et al., and Jennings and Schucker vs the data reported by Reamer and Sage.

Reamer and Sage studied the CO₂ + n-decane system in the temperature range 277.6 to 510.9 K, and in the pressure range 0.34 to 17.24 MPa. Their experimental results show a regular tendency with temperature and pressure. The solubility of n-decane in CO₂ increases as the temperature increases.

The data reported by Nagarajan and Robinson have a mean difference of 0.0022 in mole fraction; the data reported by Chou et al. have a mean difference of 0.0014; the data reported by Jennings and Schucker have a mean difference of 0.0006; and the experimental values reported in this work have a mean difference of 0.0017; all this with respect to the original data of Reamer and Sage. Then it is possible to conclude that our data compare very well with the data reported previously.

The other system selected in this work for comparison was CO₂ + n-hexadecane at 308.15 K. The solubilities reported by Charoensombut-Amon and coworkers (1986) and those

obtained in this work are shown in figure 2. The differences between the data reported by Charoensombut-Amon and our data are shown in figure 3. It can be observed that there exists good agreement between both sets of results, the mean difference is 0.0007 in mole fraction. From the comparison carried out with two different systems it is possible to conclude that the methodology and the apparatus constructed in this work are capable of producing reliable information.

There is a lot of data reported in the literature for very different systems. In figure 4 we include data previously reported for lineal hydrocarbons from n-C₁₀ to n-C₂₈ determined by different authors. In spite of the systems being very similar, i.e. the solute is a linear hydrocarbon and the solvent is CO₂ in all cases, the solubilities observed in these systems are not regular neither as a function of temperature nor as a function of pressure. In four of the systems the solubility increases as the temperature increases but in six systems the solubility decreases as the temperature increases.

In general, the solubility of the solute increases with pressure but the system CO₂ + n-decane shows an interesting behavior, e.g. in the range 444.3 to 510.9 K at low pressure, 2 to 6 MPa, the solubility decreases when the pressure increases, then in the range 6 to 12 MPa the solubility remains constant and in the range 12 to 18 MPa the solubility increases again.

According to the behavior shown in figure 4 it is very difficult to establish a clear trend in order to correlate the solubility of the solute with some physicochemical properties.

In this work we have undertaken a systematic study on the solubility of heavy lineal hydrocarbon + CO₂. The estimated uncertainties for our experimental data are ± 0.05 K in

temperature; ± 0.002 MPa in pressure; and ± 0.00005 in mole fraction. The system studied in this work is formed by n-octadecane + supercritical CO₂, Schmitt and Reid (1988) made solubility data measurements for this system earlier. Their results at 310 and 320 K are shown in figure 5 together with our experimental results, in the range 310 - 353 K. Their results show that, at a fixed temperature, the solubility increases as the pressure increases, and that the solubility decreases when the temperature increases. This behavior needs to be confirmed because they reported 3 experimental points at 310 K and only two experimental points at 320 K.

From a comparison of data we observe that at 310 K and 12 MPa they extracted four times more n-octadecane than us. While at the same temperature but at 14 MPa they extracted twice the amount of n-octadecane extracted by us. At 19 MPa they extracted 10 times more. At 320 K their results are higher than ours at 313 and 333 K. Hence, in this work it was not possible to reproduce their solubility data. We assume that our solubility data are correct due to the calibration of the measuring equipment and the consistency of our experimental results with literature data for both n-decane and n-hexadecane.

From the solubility data for n-octadecane in supercritical CO₂ obtained in this work, figure 5, as a function of pressure, it is possible to observe that for all isotherms the solubility increases with pressure in the studied range. It is easy to observe that at 310 K and 313 K the slope of the corresponding curves is greater than that observed at 333 and 353 K, it means that, the amount of solute extracted with the same change in pressure decreases as the temperature increases.

The solubility data for n-octadecane in CO₂ obtained in this work are shown in figure 6, as function of temperature. In this plot it is easy to observe that for all isobars the solubility has a large dependence with temperature and on each isobar it is possible to observe a maximum in the solubility data.

In spite of a large amount of solubility data for lineal hydrocarbon in supercritical CO₂, in a wide range of pressure and temperature, it is not yet possible to obtain general conclusions about the behavior of this type of systems. As noted by McHugh and Krukoni (1986), very different high-pressure phase behavior can occur for solid-SCF mixtures that are superficially quite similar, for instance, they compare the solubility behavior for naphthalene - ethylene system with biphenyl - carbon dioxide system. Both naphthalene and biphenyl are heavy, nonvolatile solids, with melting temperatures well above room temperature, and both ethylene and carbon dioxide are light gases at ambient conditions with relatively mild critical conditions. Then, one might expect the characteristic shapes of the solid - solubility isotherms of these two systems to be quite similar. However, the isotherms for naphthalene - ethylene exhibit a large solubility enhancement, which is sensitivity to small changes in pressure whereas the isotherms for biphenyl - carbon dioxide show that their solubility is smaller than the first mentioned system. Then, it is necessary to have at hand a lot of information in order to explain the observed behavior, information such as upper critical end points (UCEP), solid-liquid-vapor lines, etc.

McHugh and Krukoni mentioned that at low pressure a solid - liquid - gas equilibrium is obtained and depending on the concentration of the overall mixture, either liquid - gas, solid - liquid, or a single liquid phase exists as the pressure is increased. The free volume is also important because the solubility behavior is a consequence of a free - volume effect

resulting from the large disparity in size between both components among other properties. Thus, at high pressures, increasing the pressure reduces the free - volume of the supercritical fluid and hence reduces the solubility of the solute. They pointed out that the phases present in the system are very important because the solubility is very different if solid, liquid or fluid is present. Also, it is very important to be aware that a high-melting solid can melt at relatively mild temperatures when in contact with a supercritical fluid at high pressures. Then, if only solubility data are obtained it may not be possible to discern whether the solid has melted on the basis of the shape of the solubility isotherm.

Finally, it is important to be aware that for a heavy solid under the influence of a SCF, the liquid phase that is formed when the solid melts can be less dense than the SCF phase. If this density inversion occurs, the heavy liquid phase would be pushed out of the equilibrium cell by the SCF-rich phase in a flow type experiment. They mentioned that such behavior has been observed for octacosane + CO₂, included in figure 4.

Conclusions

An experimental method and an apparatus have been developed for measuring solubilities of liquids and solids in supercritical gases. Solubility of n-octadecane in CO₂ has a clear functionality with pressure and temperature. The affinity of n-octadecane in CO₂ increases as the pressure increases and the functionality with pressure shows a maximum solubility point.

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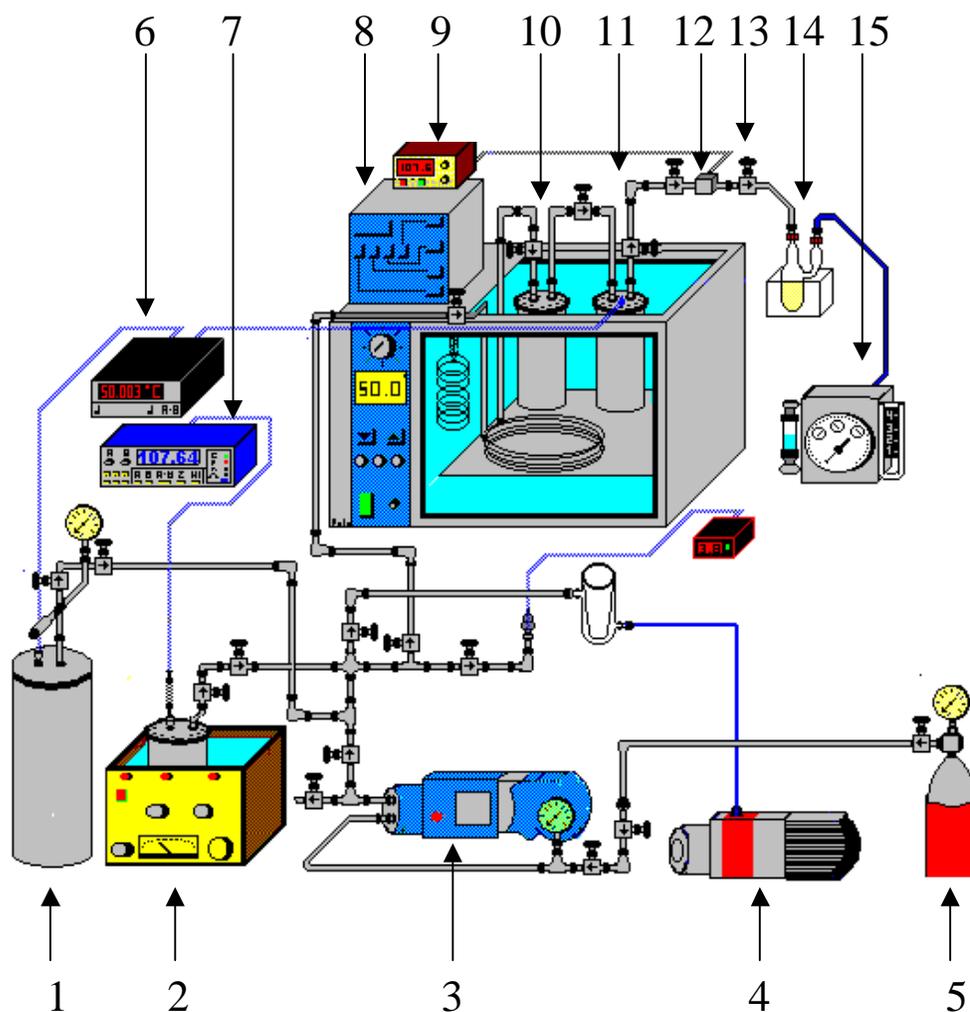


Figure 1. Schematic diagram of the semi-flow apparatus for supercritical extraction studies. 1) thermocompressor, 2) feed cell immersed in a water bath, 3) compressor, 4) vacuum pump 5) CO₂ commercial cylinder, 6) Thermometer, 7) pressure indicator, 8) temperature constant bath, 9) pressure indicator, 10) pre-saturator, 11) equilibrium cell, 12) pressure transducer, 13) micrometering valve, 14) recollection cell, 15) wet test meter.

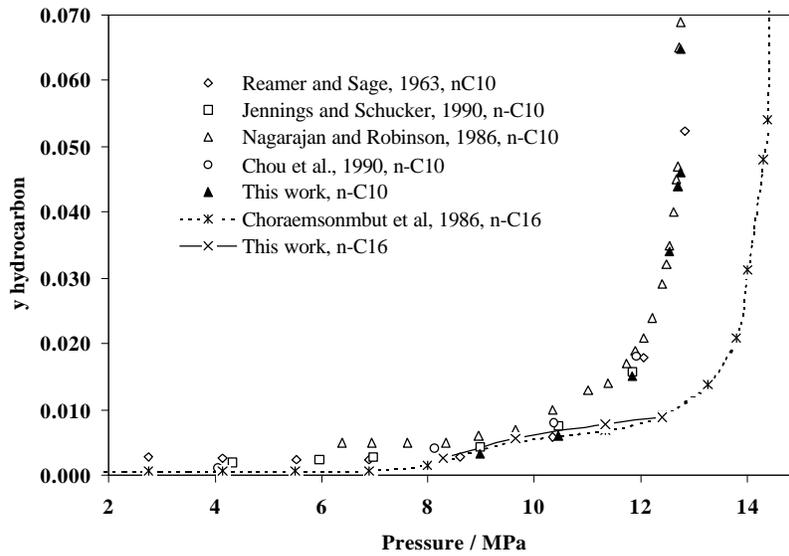


Figure 2. Comparison of solubility data from this work with literature data for n-decane in CO_2 (y_1) at 344.15 K; and n-hexadecane in CO_2 (y_1) at 308.15 K.

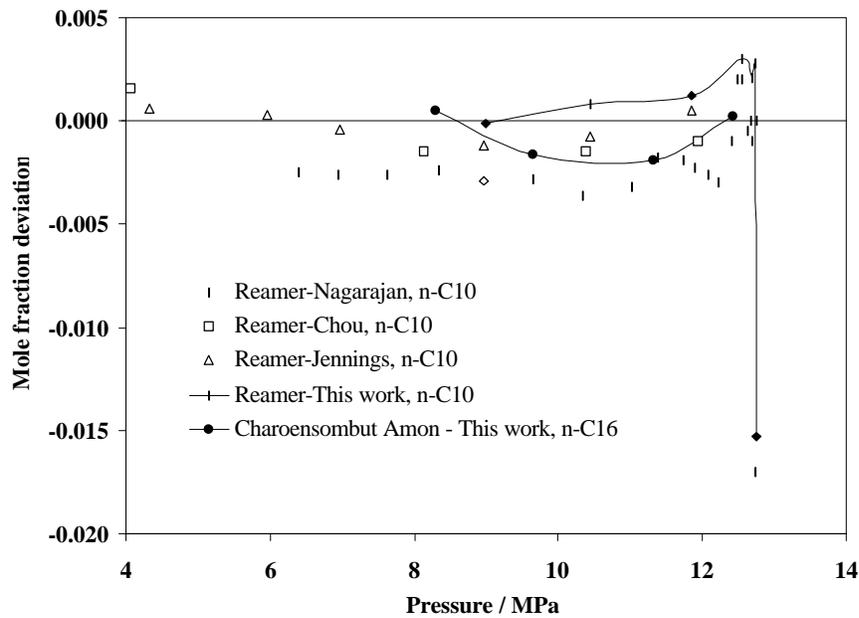


Figure 3. Differences between solubility data (from this work, Nagarajan and Robinson, Chou et al., and Jennings and Schucker) and those obtained by Reamer and Sage, n-decane at 344.15 K. And differences between this work and solubility data obtained by Charoensombut-Amon et al. for the system n-hexadecane + CO_2 at 308.15 K.

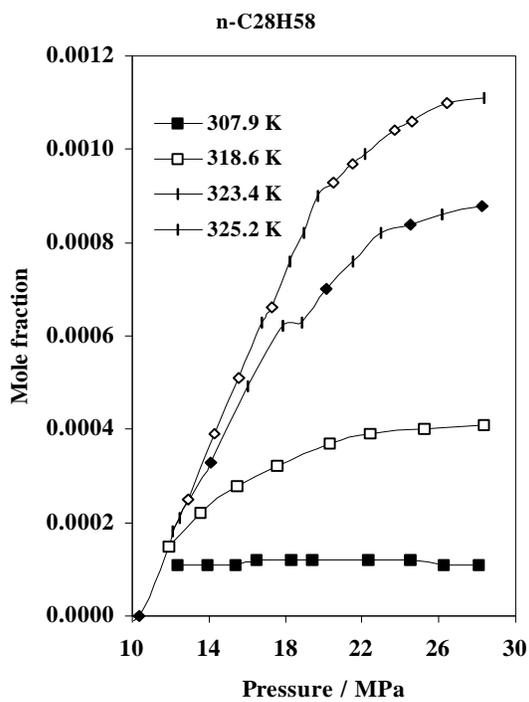
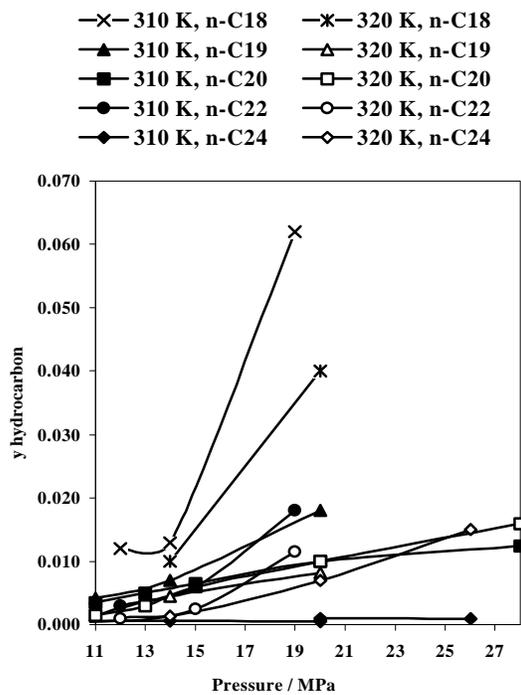
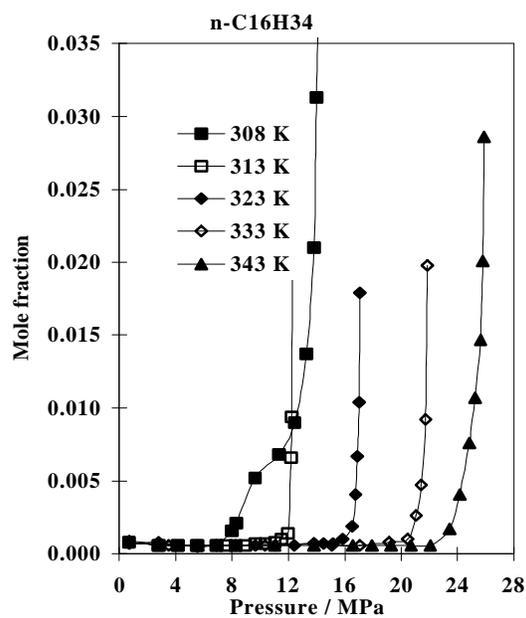
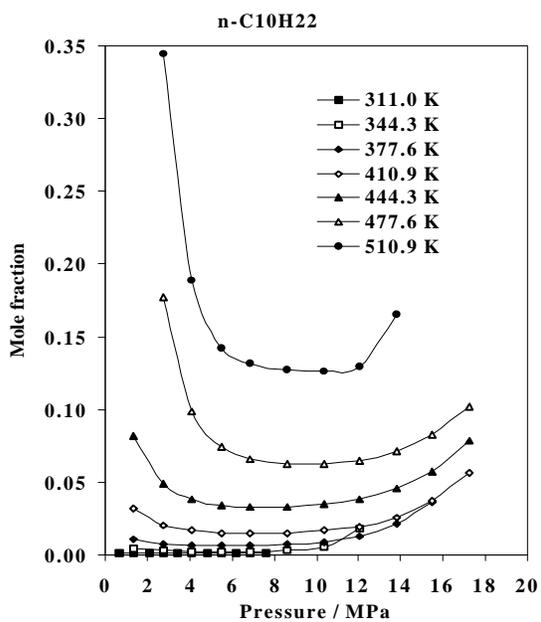


Figure 4. Published data of hydrocarbons in CO₂ at different pressures and temperatures.

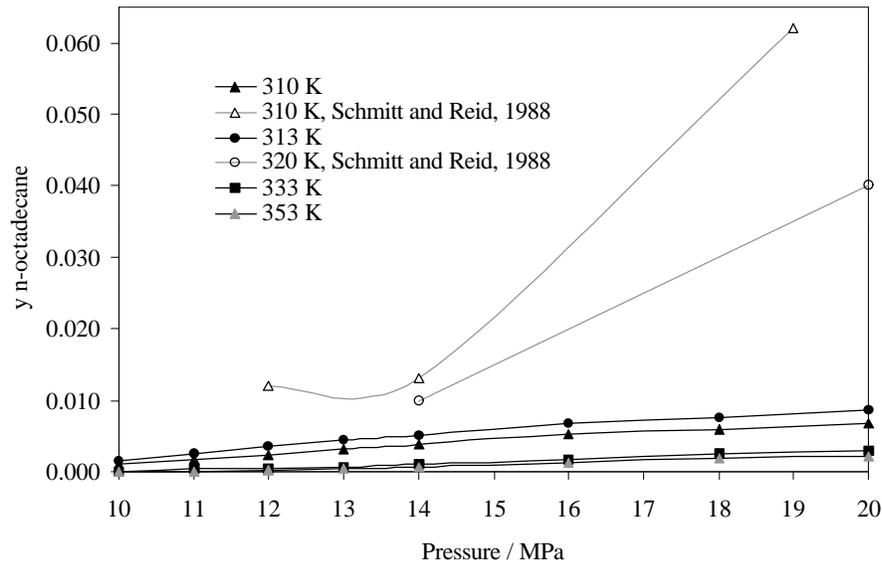


Figure 5. Comparison of solubility data from this work for n-octadecane in CO₂ with literature data.

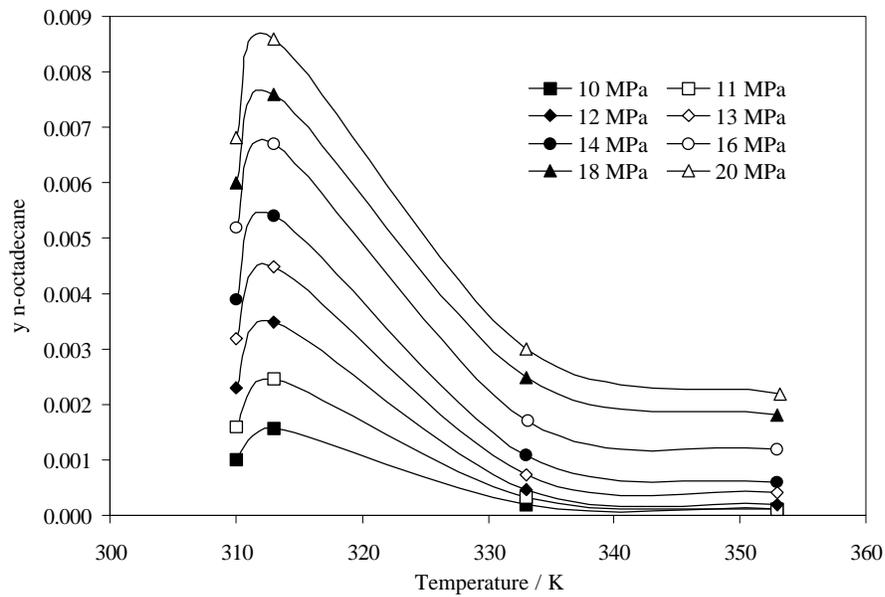


Figure 6. Solubility of n-octadecane in CO₂ as function of temperature, data obtained in this work with a semi-flow apparatus.