

A Procedure for Measuring High-Pressure Phase Equilibria by Means of a Double-Chamber Recirculation Apparatus

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ABSTRACT

An experimental method for measuring high-pressure phase equilibria of systems composed of a supercritical and a liquid phase is described. Measurements are carried out by means of a recirculation apparatus composed of two chambers: the "equilibrium cell", where a liquid phase coexists with a supercritical phase, and the "gas cell", which contains the supercritical phase only. The supercritical phase is continuously recirculated between the two chambers by means of a piston pump in order to reduce time for equilibration. Before sampling, the gas cell is separated from the equilibrium cell by closing valves, in order to avoid any disturbances of the equilibrium when reducing pressure during the withdrawal of the supercritical phase. In this way, large samples of the supercritical phase can be withdrawn. This is very important for low-solubility systems, which are common in supercritical processes. Since sampling of the phases is a crucial part of the experiments, a detailed description of the preliminary runs that allowed to fix the optimal procedure is reported. The apparatus and the proposed method have been tested on the well-known binary system Carbon dioxide + Limonene. Furthermore, some experimental data on the multicomponent system Carbon dioxide + Lemon essential oil are reported.

INTRODUCTION

Information on high-pressure phase equilibria is essential for many chemical and separation processes. In particular, experimental data on high-pressure phase equilibria are the basis of feasibility studies in the field of supercritical-fluid technology. A relevant example is represented by the separation of liquid multicomponent mixtures by means of supercritical carbon dioxide as a solvent (e.g. deterpenation of essential oils [1], fractionation of fish oil ethyl esters [2], etc.). In this context, the most important parameters to find out are:

- the solubility of the liquid mixture in the supercritical solvent, which is one of the parameters that determines the solvent to feed ratio of the separation process;
- the solubility of the supercritical solvent in the liquid mixture, which is closely related to the extent of the solvent losses of the process;
- the selectivity of the supercritical solvent with respect to a couple of key components to be separated, which affects the number of theoretical stages and the reflux ratio in countercurrent continuous processing.

Thus, measurements of the equilibrium composition of both phases (liquid and supercritical) for a multicomponent system, at various pressure and temperature values, are needed [3].

Different methods can be employed to perform high-pressure phase equilibrium measurements for systems containing one or more subcritical component and a supercritical one. Each method presents both advantages and disadvantages, depending on the particular system under investigation. For example semicontinuous methods, where the supercritical phase passes through a batch of liquid phase at constant pressure and temperature, are quite simple to perform but are more suitable for binary systems, where the variation of the overall composition does not affect the compositions of the two phases at equilibrium. On the other

hand, the use of a closed apparatus, operating at constant pressure and temperature, is appropriate for multicomponent systems, because the overall composition at equilibrium is fixed. However, if the equilibrium is established in a single high-pressure chamber, it is often impossible to sample a sufficient amount of supercritical phase without altering the equilibrium pressure. This can be a serious drawback for low solubility systems, which are typical in supercritical fluid processing, because they require large samples of supercritical phase to attain a sufficient amount of solubilized liquid for the analysis.

In this work a two-chamber recirculation apparatus for measuring high-pressure phase equilibria, designed in such a way to allow sampling of large quantity of supercritical phase without altering the equilibrium, is presented. Preliminary runs, devoted to identifying the best sampling procedure, are described. The apparatus and the proposed procedure have been employed to measure the phase equilibria of the system Carbon dioxide + Limonene at 50°C, which have been extensively studied by various authors, in order to compare the obtained results to the available literature data. Furthermore, some data on the multicomponent system Carbon dioxide + Cold-pressed lemon essential oil are also presented.

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 cm³ 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. The maximum uncertainty on pressure measurements at 50°C is ±0.3 bar. 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 supercritical phase can be recirculated between the two chambers by means of an air driven high-pressure piston pump (Haskel 4B-150). 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 supercritical 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), limonene has been purchased from Sigma-Aldrich [R-(+)-Limonene, 97%] and cold-pressed lemon essential oil is from Sicily (Simone Gatto, Italy). GC analysis on the essential oil have been performed according to the procedure described in a previous work [4]. The composition of the essential oil is expressed in terms of the three main classes of compounds and it is: monoterpenes 93.8%, oxygenated compounds 4.2%, sesquiterpenes 2.0% (by weight).

EXPERIMENTAL METHODS

At the beginning of each experimental run approximately 20 g of limonene or of cold-pressed lemon essential oil are fed to the chamber C1, also called 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, also called 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 supercritical phase is continuously recirculated from the gas cell to the equilibrium cell, in order to reduce time for reaching the equilibrium condition. Pressure oscillation induced by the pump on the system ranges from 0.05 bar, at the higher pressures, to 0.4 bar at the lower pressures.

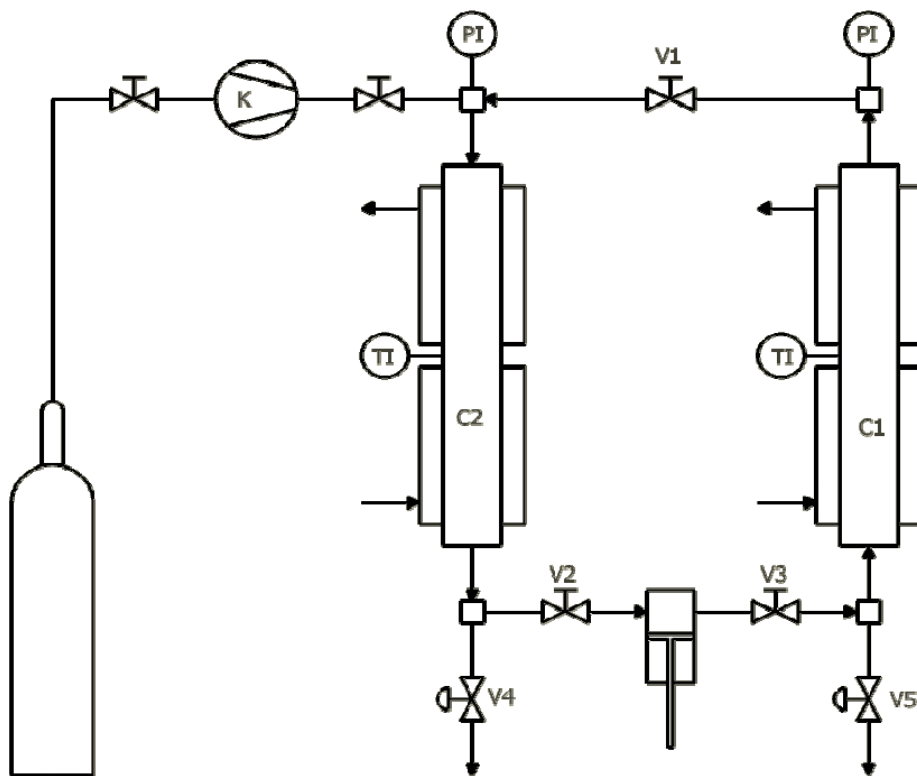


Figure 1: Apparatus for high-pressure phase equilibrium measurements. C1: Equilibrium cell; C2: Gas cell; V1, V2, V3: closing valves; V4, V5: high-pressure micrometer valves; K: membrane compressor.

Some preliminary runs allowed to define a reasonable value for the number of pump cycles per minute and the duration of the recirculation period. A value of 60 cycles per minute for a 6 hour duration has been fixed. 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 solubilization 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 3 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 supercritical 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^3 . Thus, it is possible to get a large amount of the supercritical phase and, as a consequence, a sufficient amount of solute for the analysis. This is noteworthy for systems of interest in supercritical processing because liquid solubility in supercritical carbon dioxide is typically low.

Sampling of the phases is one of the major problems related to high-pressure phase equilibrium experiments. For this reason, a number of preliminary runs was performed in order to identify the best procedure. As for supercritical phase sampling, the procedure that gave the best results is the one described as follows. At first the pressure of the gas cell is reduced 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 . 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 $0.6 - 4.5 \text{ g}$ in the equilibrium

measurements) is determined gravimetrically, whereas the volume of the gas exiting the sampling flask is measured in a gas flow meter. In order to determine the total amount of carbon dioxide in the cell C2 at equilibrium, the moles of CO₂ that flows through the flow meter are added to the moles that remains in the cell at the end of 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 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 equilibrium experiments have showed that 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. Three preliminary runs validated the above-mentioned procedure. In these runs the gas cell C2 was loaded with a known amount of limonene: 1.70, 1.79 and 1.44 g, respectively. Subsequently the cell was taken to the desired temperature and carbon dioxide was fed to such a pressure value that a homogeneous phase is doubtless expected. The gas cell was maintained isothermal and closed for about 1 hour and then the above-mentioned sampling procedure was applied. At the end of the washing step, the amount of limonene recovered resulted to be: 1.70, 1.76 and 1.44 g, respectively, which is to say an average recovery equal to 99.4%.

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 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 a gas flow meter. The sampling procedure lasts until approximately 1 litre of carbon dioxide is measured (at atmospheric pressure and ambient temperature). This value has been selected taking into account two contrasting factors: a large volume sampling 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 0.5 – 2.1 g and in a pressure lowering below 1 bar. These values have been considered reasonable.

Another preliminary run was designed to further validate the whole procedure. The chamber C1 was loaded with 58.18 g of limonene and the double-chamber system was pressurized up to 12 MPa. In this condition, a homogeneous phase is doubtless expected. By using the thermodynamic model described in a previous work [1], it is possible to calculate that carbon dioxide molar fraction is equal to 0.915. The supercritical phase was recirculated between the two chambers by means of the piston pump (60 cycle per minute, 6 hours). After the recirculation period, the sampling from the cell C2 and C1 was carried out according to the above-mentioned procedure. If the whole procedure is coherent, the composition value determined from sampling the chamber C2 must be approximately equal to the value from the chamber C1; furthermore, both values must be close to the model prediction. The sampling of the cell C2 and C1 led to carbon dioxide molar fraction equal to 0.919 and 0.912, respectively. These values appear to be reasonably consistent with the expectations.

RESULTS AND DISCUSSION

The experimental method has been validated on experimental phase equilibrium data referred to the binary system Carbon dioxide + Limonene. This system has been selected because of the availability of several literature experimental data to compare with [5-13]. All the experimental runs have been carried out at 50°C. Experimental pressure ranges from 8.5 to 10.1 MPa. According to the above-mentioned procedure, experimental measurements of both supercritical and liquid phase have been carried out. The solubility of limonene in the supercritical phase is shown in Fig. 2. Except for the runs at 8.8 and 10.1 MPa, the measurements of the supercritical phase composition have been performed twice for each pressure. In these cases, the reported value in Fig. 2 is the average. The average relative deviation of these measurements is 1.4% (with respect to the average solubility value) that is to say that reproducibility is very good. As it was expected, the solubility of limonene in the supercritical phase increases as pressure increases, rising from 17.5 g/kg at 8.5 MPa up to 79.4 g/kg at 10.1 MPa. Fig. 2 also shows that data measured in this work compare well to literature data in the same pressure range. This consideration takes into account that the typical discrepancies between different authors are quite large, when performing these kind of measurements, as shown by Fig. 2. Some marked discrepancies on solubility values are apparent at higher pressure values (above 9.6 MPa), when the two phases are approaching the critical point. In this region, data of this work are consistent with those of Chang and Chen [8], whereas the solubilities found in two other works [9, 13] are higher. However, it should be noted that the solubility in this region is difficult to assess because of its marked variation in response of small pressure variations. In fact, it is remarkable that the same solubilities found in two of the above-mentioned works [9, 13] are obtained in the present work at pressures only 0.2 MPa higher. As for the liquid phase, Fig. 3 reports carbon dioxide molar fractions found by experiments. In this case, each measurement has been performed once. The experimental data of this work are in good agreement with those of Akgün et al. [7], whereas they underestimate the other available literature data on the liquid phase.

In addition, some experimental measurements have been carried out on the multicomponent system Carbon dioxide – Lemon Essential Oil (LEO), which is a complex natural mixture of several compounds. Both the solubility of the natural oil in the supercritical phase and of carbon dioxide in the liquid phase have been measured at 50°C, at the same pressure values than those selected for the runs on limonene. Furthermore, the composition of the extracted

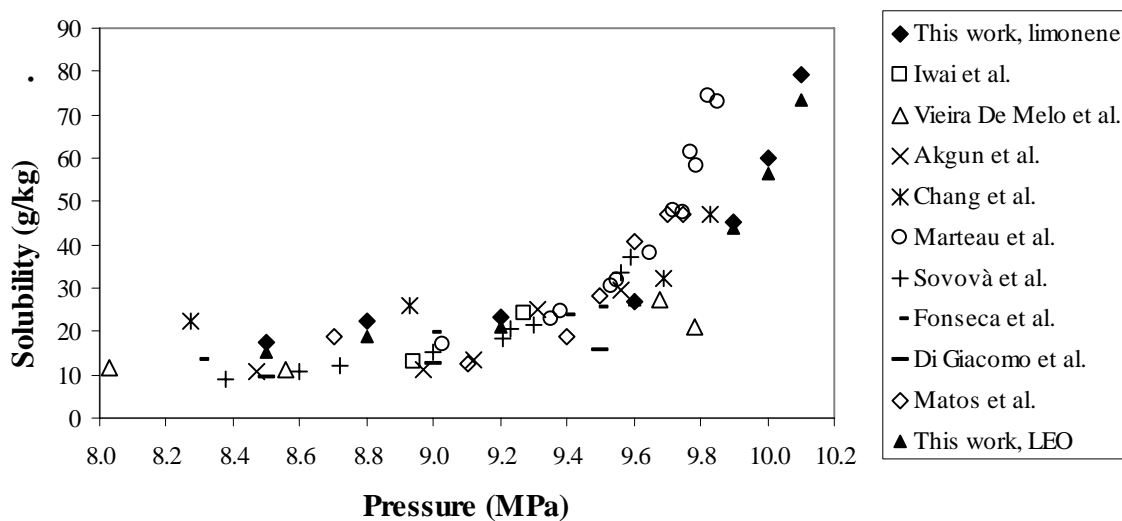


Figure 2: Solubility of limonene and lemon essential oil in the supercritical phase at 50°C. Values are expressed as gram of limonene per kg of carbon dioxide.

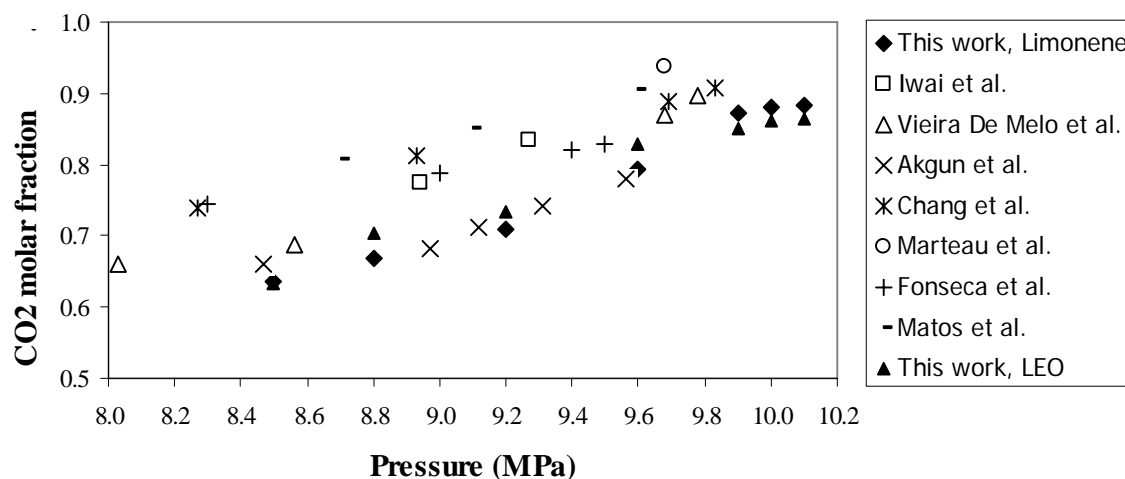


Figure 3: Carbon dioxide molar fraction in the liquid phase. Data report equilibrium composition at 50°C.

oil has been determined by GC analysis. For each pressure value a single experimental run has been performed. The extracted oil composition is the average of three GC repetitions. The solubility of the oil in the supercritical phase is slightly lower than those of pure limonene. Since LEO is mainly composed of monoterpenes (94% by weight), such as limonene and similar compounds, whereas the small remaining part of the oil is composed of heavier compounds, these data are consistent with the expectations. As for the solubility of carbon dioxide in the liquid phase, it can be noted from Fig. 3 that limonene and lemon essential oil show the same feature. As for supercritical phase composition on solvent free basis (the extract), at the following experimental pressures: 8.5, 8.8, 9.2, 9.6, 9.9, 10.0, 10.1 MPa, the mass fraction of oxygenated compounds is reduced from 4.2% (the feed oil) down to 0.78, 1.87, 2.02, 2.70, 2.92, 2.94 and 4.17%, respectively.

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