Investigation of High-Pressure Phase Equilibrium with the Observation of the Cloud Point

Introduction

In the last 2 decades supercritical solvents have had a more significant role as the solvents in chemical reactions. In fact a significant number of high-pressure reactions in the gas phase (e.g. synthesis of ammonia, methanol or polyethylene) are performed under supercritical conditions. The large-scale manufacture of these products has been executed for several decades, thus the necessary chemical and mechanical engineering experience was obtained to permit the safe design and operation of high-pressure equipment. The effect of a supercritical fluid (the solvent, the reactants, or the whole system is above critical point) on chemical reactions has been studied since the beginning of the 1970s. The number of publications dealing with this subject increased dramatically in the 1980s, and additionally to extraction and chromatography a new field of application of supercritical fluids evolved.

If a chemical/biochemical reaction is carried out in a supercritical solvent (generally carbon dioxide or water), it clear advantages. One possibility is that the reaction, which was previously carried out in halogenated or other toxic organic solvents, can be performed in supercritical solvents with the same or better selectivity and reaction rate. This way VOC (volatile organic compound) emissions can be reduced significantly, which is an important issue both environmentally, and economically. Loss of VOC during the processing can be significant, however only the in case of expensive solvents is the economy of solvent recovery the main driving force of substitution. Ofter only a new technology can meet the increasingly strick emission limits. Another reason of application is if during the downstream processing the whole manufacturing procedure can be more economical due to the use of supercritical solvents.

The benefits of supercritical solvents are that the properties of the solvent (solubility, diffusion coefficient, mass transfer coefficient, etc...) can be modified with two independent and easily-controllable parameters, the pressure and temperature. Thus, the reaction can be optimized to reach the maximal selectivity and/or reaction rate. In the case of carbon dioxide ($P_c=73.8$ bar, $T_c=31 ^\circ C$) the quantity and quality of the co-solvent, which is typically added to the system in 1-10 %, is normally included in the variable parameters. Another important advantage over the conventional solvents is that the previously soluble substance precipitates after depressurization. In the case of carbon dioxide the solvent is gaseous under standard conditions, thus if the product is not gaseous (typically liquid or solid), then the solvent leaves the substance. In the case of water the separation of the product and the solvent is also simple because the sub and supercritical water ($P_c=220$ bar, $T_c=374 ^\circ C$) is nonpolar, while at atmospheric conditions it is a polar solvent. Thus the components soluble in supercritical water have a poorer solubility in water at room temperature and atmospheric pressure, and the substances soluble in water under normal circumstances are slightly soluble in supercritical water.

The major drawback of using supercritical solvents is the relatively high pressure applied during the process (80-500 bar). In certain industries this pressure range is generally accepted and frequently applied (e.g. the polymer industry). Currently in other sectors such as fine chemical and pharmaceutical industry it is rarely used. However, high-pressure devices can be found in every
analytical laboratory, e.g. the operating range of a standard HPLC (high performance liquid chromatograph) covers the 80-500 bar pressure range applied in processes using supercritical fluids.

**Fundamentals**

Liquefaction of gases under pressure occurs only below critical temperature, which depends only on the quality of the substance. The pressure, which should be applied at the critical temperature to condense the gas, is called the critical pressure. If the substance is heated above critical temperature and compressed with higher pressure than the critical pressure, the material remains homogeneous. This is called the supercritical fluid state, and is a state in which the properties of the material are between the properties of the liquid and gaseous fluid states.

![Carbon dioxide phase diagram](image)

**Fig. 1.** Carbon dioxide phase diagram

Figure 1 shows the P-T phase diagram of carbon dioxide. On the diagram the solid, liquid and gas phases can be seen that are separated by the melting, boiling and sublimation curves. The critical point is indicated by C. The area representing the supercritical fluid state is bounded by dashed lines. Crossing the dashed lines no change of phase occurs, the changing of physical properties is continuous. This can be also observed on the density curves which change continuously.

**The Aspects of Selection of Supercritical Solvents**

The selection of the solvent plays an important role in every aspect of chemical operations, like extraction, reactions, crystallization or analytical processes. The conditions (pressure and
temperature) are determined by the critical parameters of the solvent. Supercritical fluid extraction can be feasibly applied to numerous substances that are solid or liquid at room temperature and pressure. The general selection criteria for the traditional solvents are also valid in this case (e.g. good solvent power, easily available, cheap, not toxic, not harmful to the product and environment and not flammable).

Carbon dioxide is favoured as a solvent in supercritical operations for the following beneficial properties:

- It is not harmful to health, thus it is well applicable for the production of medicines, food and consumer goods.
- It has a high density, thus solubility of non-polar materials is sufficiently high.
- Carbon dioxide does not react with the treated material.
- It has low critical temperature (31°C), thermal degradation can be minimized.
- It is non-flammable and non-corrosive.
- It is available in large quantities and in a purity required in the food industry.
- CO₂ is environmentally friendly.
- After extraction it can be removed from the product without any residue.
- The solvent power can be influenced by modifying the pressure and temperature of the supercritical solvent.

However generally only non-polar molecules can be dissolved in the non-polar carbon dioxide. The solvent power can be improved by applying mixed solvent or co-solvent, ethanol for example. The critical point of the mixture can be modified significantly by small quantities of co-solvent (Figure 2). Table 1 shows the effect of small amount of ethanol in carbon dioxide for the critical point of the mixture.

Table 1: The effect of ethanol on the critical point in carbon dioxide

<table>
<thead>
<tr>
<th>ethanol content [mol%]</th>
<th>Tc [°C]</th>
<th>Pc [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>31.3</td>
<td>73.8</td>
</tr>
<tr>
<td>1</td>
<td>32.7</td>
<td>76.6</td>
</tr>
<tr>
<td>2</td>
<td>35.7</td>
<td>78.3</td>
</tr>
<tr>
<td>4</td>
<td>40.5</td>
<td>84.3</td>
</tr>
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</table>
Fig. 2: The critical points of the ethanol-carbon dioxide mixture. Every coherent temperature-pressure points belong to different compositions. The critical points of the pure components are marked with points.

**Cloud point**

When the solution becomes oversaturated due to pressure reduction it becomes visibly cloudy and foggy, known as the cloud point. The cloud point is characterised by the composition, pressure and temperature. The pressure and temperature in the cloud point at given composition is obviously lower than the critical pressure and temperature. This phenomenon can be observed in Figure 3, where the phase diagram of the CO$_2$-ethanol system can be seen at 100 °C (component 1 is CO$_2$).

The purpose of the laboratory exercise is to observe the pressure values when the phase separation occurs at different temperatures and at two different compositions.
The isothermal change at constant concentration is signed by the arrow. Cloud point occurs when entering the two-phase area.

**The measurement**

During the experiment the cloud point values of mixtures of carbon dioxide and a chosen solvent (e.g. ethanol, acetone or methanol) will be observed at several different temperatures and two different concentrations. The measured cloud point pressures against composition values have to be plotted in a common diagram with literature data and with equilibrium data calculated by equation of state at constant temperatures. A schematic diagram of the high pressure equipment used during the measurement is shown in Figure 4. The front wall of the cell is a pressure-resistant sapphire window. The back wall is a movable piston. During isothermal conditions the pressure in the inner space is controlled with changing the volume of the cell. The density of the homogeneous mixture has to be also determined.
Fig. 4: A schematic drawing of the high-pressure optical cell used for measurement.

After writing the test, the group will be divided into two (group /I and group /II), so that everyone will have the opportunity to use the device.

Before starting measurements, group /I determine the exact steps of weighing with the help of the measurement team leader.

The steps are the following:

- Selection of the solvent.
- Select the first weighing concentration using the isothermal phase diagrams available (conditions: cloud point pressure should be well-measurable in the 35-45 °C or 45-60 °C temperature range, the solution has to be diluted. Choice of temperature range is your task.).
- Determine the weight of the solvent to be weighed (minimal volume of the cell 44 mL, the pressure is chosen by you, but it must be in the homogeneous phase, the density belonging to the chosen pressure has to be read off).

Meanwhile group /II become acquainted with the cell and observe the critical point of carbon dioxide. While group /I after finishing the calculations perform their task, group /II calculates the maximum dilution and the possible composition.

The steps are the following:

- The starting point is the data calculated by group /I.
• Determine the cell volume if the planned amount of substance is heated to 45 °C and the pressure is 5 bar above the cloud point pressure.
• The solution can be diluted up to 60 mL at constant pressure with pure carbon dioxide entering the cell, based on this the dilution and the second planned composition can be determined.

The tasks of group /I:

• Weight the calculated amount of solvent with pipette, but the weight of the solvent has to be determined.
• Close the cell, thermostat the cell at the planned temperature and refilling the cell at the planned volume at the planned pressure.

The amount of loaded CO₂ is measured. For this purpose a cooled CO₂ syringe pump is available.

Refill the dosing pump with carbon dioxide and cool so that the carbon dioxide is in liquid phase in the piston (the data can be read off on the phase diagram of the pure carbon dioxide) The liquid has significantly lower compressibility than the supercritical fluid therefore the measurement is more accurate if carbon dioxide is in liquid phase in the piston.

Set the desired pressure on the dosing pump. This pressure should be 10-50 bar higher than the planned pressure of the cell.

Ensure a steady state has been reached inside the pump; steady-state has been achieved if the pressure and volume values on the display of the pump no longer change. Then write the volume, the temperature and the pressure of the pump and then start filling the cell.

At first feed some carbon dioxide the cell and move the piston forward (minimum volume of the cell). Fill up the cell to the planned pressure while continuously monitoring the phases (and recording the observations) then set the prescribed volume (at constant pressure). Then you shall see homogeneous phase in the cell. Write down the volumes from the dosing pump.

The mass of the weighed carbon dioxide can be calculated from the displacement of the piston of the dosing pump (volume reduction) and the density of carbon dioxide at the set pressure and temperature in the piston.

• Measure the pressure of cloud point of the solution at 3 different temperatures. Each group member should measure at least 3 points. Observe the phenomenon of cloud point while increasing the volume of the cell, write down the pressure, temperature and volume measured at phase separation. After phase separation start slowly decreasing the cell volume and write down the pressure, temperature and volume values when the two phases become homogeneous again (the density of the solution will be calculated from these data).
• Choose the best equation of state and interaction parameters for the temperature values planned by group /II from the isotherms illustrated by group /II with the help of the PE2000 program. Prepare the complete phase diagram with the use of GPEC program. Get acquainted with the operation of the program and observe whether the calculated model predicts the expected phase behaviour.
• Calculate the composition in mole fraction (the more volatile compound is carbon dioxide) of the solution, which group/II measures in the cell after dilution (check the original composition calculation!). Read the cloud pressure values calculated by the model for each measured data (composition and accurate measured temperature).

The tasks of group /II:

• Give the data of the given mixture (in every temperature values the equilibrium compositions of liquid and vapour phases in mole fraction of the more volatile compound, the carbon dioxide) received from literature to the PE2000 program. With the interaction parameters from the literature let the model calculate the isotherms. Illustrate all data and curves from model results in a single diagram and save it as an image. The diagram has to be attached to the report. Select the best fitting model and its parameters in the temperature range applied in the measurements of group /I.

• Calculate the concentration of the solution measured by group /I based on the weighing data (mass fraction and mole fraction of the more volatile component).

• Create the complete phase diagram with the chosen model and model parameters in the GPEC program and read the cloud pressure values calculated by the model at the measurement points (exact temperature values and composition) applied by group /I. Also read the calculated density belonging to the homogenous phase (pressure, composition, temperature).

• When group /I carried out the measurements, perform the dilution of the solution (according to plan, but modification might be needed according to the actual weighing of group /I).

Measure the amount of loaded CO₂. For this purpose a thermostated syringe carbon dioxide dosing pump is available.

Fill the dosing pump with carbon dioxide is necessary and thermostat so that the carbon dioxide is in liquid phase in the piston (data can be read from the phase diagram of pure carbon dioxide). The liquid has significantly lower compressibility than the supercritical fluid therefore the measurement is more accurate if carbon dioxide is in liquid phase in the piston.

Set the desired pressure on the dosing pump. This pressure has to be 10 to 50 bar higher than the planned pressure in the view cell.

Adjust the filling system into steady state till the carbon dioxide inlet valve of the cell. The steady-state is set, if the pressure and volume values on the display of the pump no longer change. Make sure that pressure in the view cell is lower than the pressure in the syringe pump! Write the volume, the temperature and the pressure of the pump and then start filling the cell. The solution in the cell shall be always homogeneous. Set the required volume while loading carbon dioxide to the cell (constant pressure). Write the volume read on the dosing pump.

The mass of the weighed carbon dioxide can be calculated from the displacement of the piston of the dosing pump (volume reduction) and the density of carbon dioxide at the set pressure and temperature in the piston.

• Measure the pressure of cloud point of the solution at 3 different temperatures. Each group member should measure at least 3 points. Observe the phenomenon of cloud point while
increasing the volume of the cell, write down the pressure, temperature and volume measured during phase separation. After phase separation start decreasing the cell volume and write down the pressure, temperature and volume values when the two phases become homogeneous again (the density of the solution will be calculated from these data).

**Calculation**

For the calculations two software packages, the Phase Equilibria 2000 (PE2000) and the Global Phase Equilibrium Calculations (GPEC) programs will be used. The PE program is suitable for the combined illustration of the theoretical curves calculated with the chosen equation of state and the experimental data (data of the equilibrium compositions of liquid and gas phases at given temperature and pressure). At first, experimental data from literature and the function calculated with the interaction parameters on the given temperature of state equation from literature. Evaluate the goodness of fit.

Let the GPEC program calculate the phase equilibrium curve with the interaction parameters considered good in a wide pressure and temperature range. The GPEC program is suitable to read off the cloud pressure calculated by the model at the known composition and temperature, which will be needed to prepare the record.

Models used [Kemény S., Thury É., Deák A.: Állapotegyenletek fázisegyensúlyok számítására, BME, 1991]:

At the calculation of equations of state the initial condition is always that in equilibrium, the chemical potentials of the components in each phase are equal. The chemical potential is not a measurable parameter; it is calculated from the fugacities. The fugacity depends on the pressure, the temperature and the mole fraction. For the calculations two (or one of them) equations of state will be used. Both of them are based on dense gas model. These are the Peng-Robinson and Soave-Redlich-Kwong models which will be applied with using the van der Waals mixing rule. They are in principle suitable for calculation of vapour phase mixtures of non-associating molecules and liquid phase mixtures of non-polar molecules in a relatively wide pressure range. The interaction parameters \((k_{ij}, l_{ij})\) are mostly temperature dependent.

The Peng-Robinson equation of state:

\[
P = \frac{R \cdot T}{V - b} - \frac{a}{V^2}
\]

\[
a = \sum_{i} \sum_{j} a_{ij} z_i z_j
\]

\[
b = \sum_{i} \sum_{j} b_{ij} z_i z_j
\]

where \(P\) is the pressure (Pa), \(R\) is the universal gas constant, \(T\) is the temperature (K), \(V\) is molar volume (\(m^3/mol\)), \(a\) and \(b\) are coefficients, \(i\) and \(j\) are components, \(z_i\) is the mole fraction of component \(i\).

The Soave-Redlich-Kwong equation of state (Redlich-Kwong equation of state modified by Soave, where \(a\) depends on \(T\)): 
\[ P = \frac{R \cdot T}{V - b} - \frac{a}{V(V + b)} \]

\[ a = \sum_i \sum_j a_i(T) z_i z_j \]

\[ b = \sum_i \sum_j b_{ij} z_i z_j \]

\[ a_i(T) = 0.4274 \frac{R^2 T^2}{P_C} \left[ 1 + (0.48 + 1.57 \sigma - 0.176 \sigma^2)\left(1 - \sqrt{T_i}\right)^2 \right] \]

\[ \sigma = -\log \left( \frac{P(T_r = 0.7)}{P_C} \right) - 1.0 \]

Where addition to the above \( \omega \) is the asymmetry factor, \( T_r \) is the reduced temperature (ratio of the actual and the critical temperature), the critical point is indicated by the index C.

The mixing rules can be the Van der Waals mixing rules:

\[ a_{ij} = \sqrt{a_i a_{jj}} \left(1 - k_{ij}\right) \]

\[ b_{ij} = \frac{b_i + b_{jj}}{2} \left(1 - l_{ij}\right) \]

The interaction parameters \( k_{ij} \) and \( l_{ij} \) are determined by the function fitted on the experimental phase equilibrium measurement data.

**Report**

It has to contain:

- the comparison of the measured and calculated data and the evaluation of the differences
- diagram created with the PE2000 program (the own measurement points has to be also marked)

If necessary the details of the measurement and report will be discussed with the leader of the group during the measurement.

The report can be submitted on paper or electronically (sz-edit@mail.bme.hu, pdf format). In case of electronic submission the measurement sheet containing the original measurement data has to be submitted on paper. Please indicate on the submitted paper it that the report was submitted electronically (also give your e-mail address the report was sent).

**Measuring table:**

Measuring the critical point of carbon dioxide (approximately 6 rows)

<table>
<thead>
<tr>
<th>( P ) (bar)</th>
<th>( T ) (°C)</th>
<th>Observation</th>
</tr>
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</table>

1. Measurement
   - Mass of weighed solvent (m):
   - Mass of weighed carbon dioxide (m\(_{\text{CO}_2}\)):

\[ C_i P - R \cdot T = \sum_i \sum_j C_{ij} P^i \left(1 - \frac{T}{T_r}\right)^j \]
Pump

T:
P:

Initial volume:
Volume at the end of filling:

Density of carbon dioxide:

Composition of weighed solution:

Mass fraction:

Mole fraction:

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>T (°C)</th>
<th>V (mL)</th>
<th>Observation</th>
<th>Calculated pressure (bar)</th>
<th>Measured density (in case of homogenous phase!)</th>
<th>Calculated density</th>
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Number of rows: 6 per person

2. Measurement

Before dilution

P:
T:

Mass of carbon dioxide added to the mixture (m_{CO2}):

Pump

T:
P:

Initial volume:
Volume at the end of filling:

Density of carbon dioxide:

Composition of the diluted solution

Mass fraction:

Mole fraction:

<table>
<thead>
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<th>P (bar)</th>
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<th>V (mL)</th>
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Number of rows: 6 per person

The density of carbon dioxide should be retrieved from the database of NIST Chemistry Webbook (http://webbook.nist.gov/cgi/inchi/InChI%3D1S/CO2/c2-1-3) (fluid properties; select the units of measurement, temperature and pressure range, then press for data).

Written by Edit Székely, 2012/2013 I semester