PHASE BEHAVIOR (S-L-G) AND FLUIDDYNAMIC PROPERTIES OF HIGH VISCOUS POLYETHYLENE GLYCOLS IN THE PRESENCE OF COMPRESSED CARBON DIOXIDE

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INTRODUCTION

Polyethylene glycols (PEGs) are widely used as additives for formulations and encapsulation of life science and pharmaceutical products. Moreover, due to their polarity and solubility behavior, they are proposed as carrier systems for liquid catalysts in supercritical media. Additional PEGs can be designed with tailor-made morphologies and sizes by supercritical spray processes [1].

The processes mentioned above require the knowledge of thermo- and fluiddynamic properties in presence of supercritical fluids. In the past seven years the authors performed detailed studies on phase behavior, solubility, diffusion coefficients and viscosity of PEGs in the presence of different supercritical gases [2], [3]. Meanwhile the experiments have been extended to high viscous PEGs. Both the new experimental methods for measuring solubilities and transport properties as well as the results for PEGs (6000, 8000, 9000, 12000, 20000 and 35000 kg/kmol) will be presented. The measurements were carried out at temperatures from 40°C up to 120°C and pressures from 1 bar up to 350 bar. Solubility data of compressed carbon dioxide in PEG were obtained by two different methods: through sampling out of an autoclave and by means of a magnetic suspension balance. The results are compared and the field of application of each method to study polymers at elevated pressures is pointed out. The diffusion coefficients of CO_2 in the polymer melts have been determined by sorption measurements from the magnetic balance. Furthermore the viscosity of the gas-saturated liquids has been measured using a quartz viscometer and a shear-thinning effect has been observed. The experimentally obtained results will be shown on the example of the binary mixture PEG 6000-CO_2.

EXPERIMENTAL SECTION
### High-pressure view cell

Figure 1: High-pressure cell

Figure 1 shows the view cell, which is used to observe the phase behavior of the mixture and the decrease of the melting temperature due to the dissolved gas. The cell is designed to operate up to 500 bar and 350°C. Two high-pressure windows are mounted at opposite sides to observe the phase behavior. A magnetic stirrer, which allows achieving phase equilibrium quickly, is mounted below the cell. **Figure 2** shows a schematic plot of the plant components.
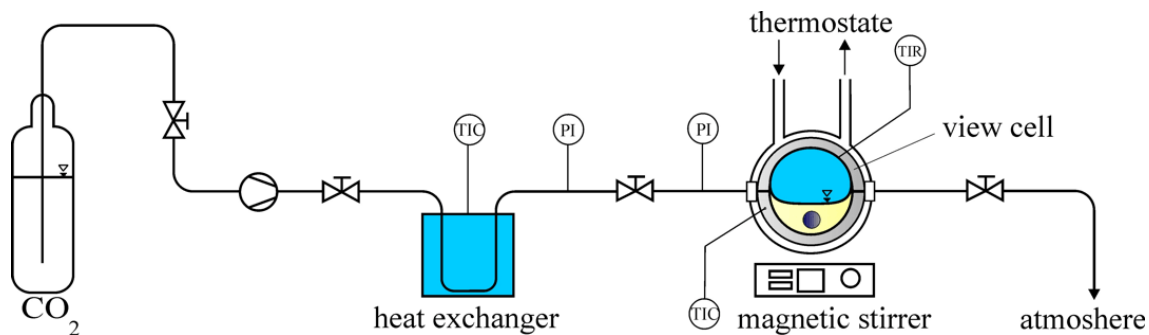
Figure 2: High-pressure cell apparatus

Autoclave apparatus

The autoclave, which is shown in **Figure 3**, allows to determine compositions of the gas and liquid phases at pressures up to 400 bar and at temperatures up to 250°C. The mass fractions of both phases were measured by a static analytical method by taking samples from the autoclave. A bellow, which is mounted at the top of the autoclave and connected to a screw press, provides an isochore displacement of the gas during the sampling. A quartz viscometer (Flucon), placed at the bottom of the autoclave, is used to measure the viscosity of the gas saturated polymer melts. The main part of this device is an oscillating quartz, which is activated to torsional vibrations and is attenuated by the viscous properties of the liquid. The viscometer allows determining viscosities in the range from 1 mPas to 100 Pas.
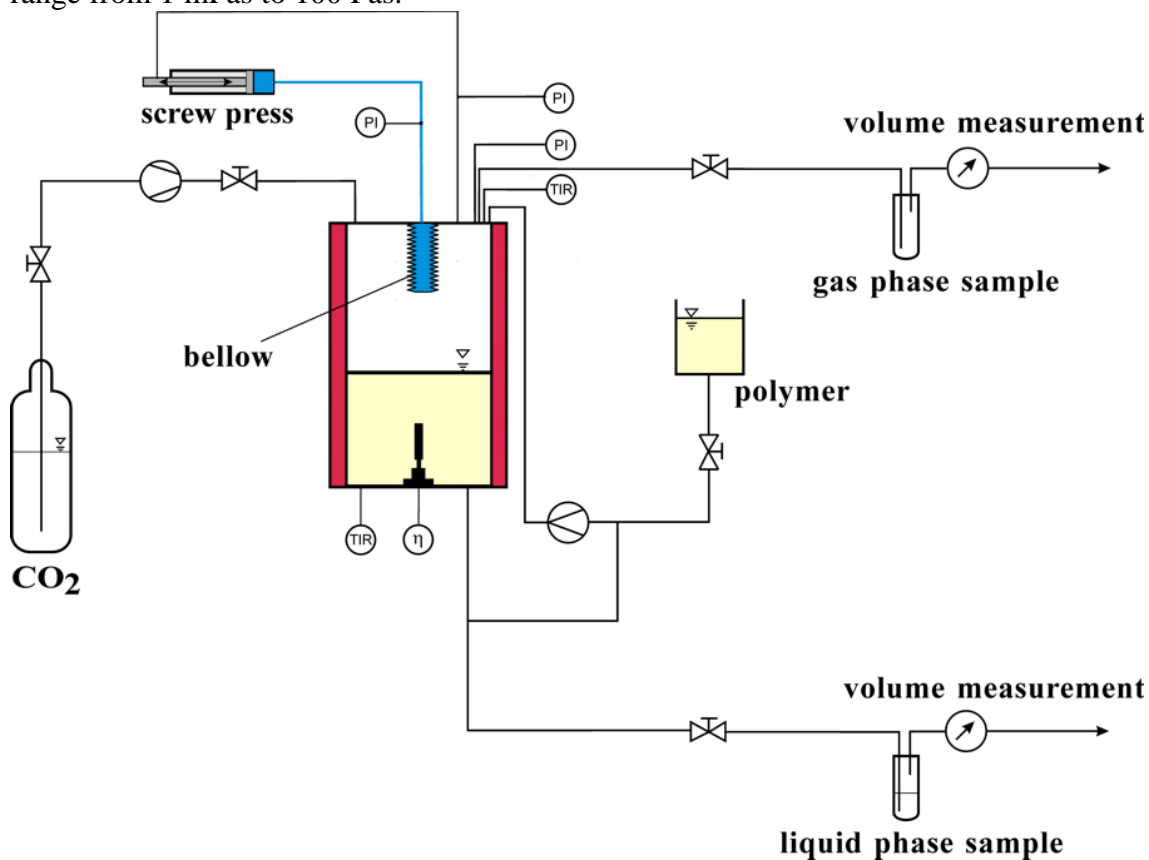
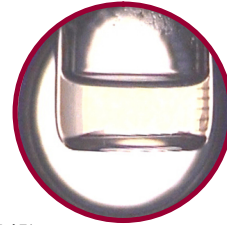**Figure 3**: Autoclave apparatus for solubility measurements

Magnetic suspension balance

Figure 4: View cell used for the the magnetic suspension balance
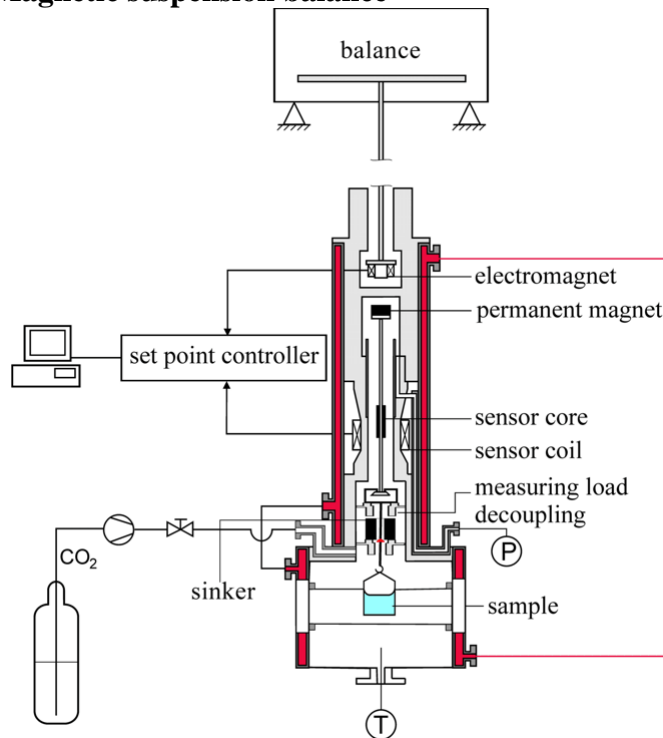
Figure 5: Magnetic suspension balance (Rubotherm, Bochum [4])

The solubility and the diffusion coefficients of carbon dioxide in PEG were obtained in a high-pressure cell with an integrated magnetic suspension balance. The cell, which is shown in Figure 4, is designed for pressures up to 500 bar and temperatures up to 350°C. The windows at the opposite sides allow taking pictures of the sample in the cell and monitoring the swelling of the polymer due to absorbed gas.

The balance itself, which is shown in **Figure 5**, is completely separated from the content of the cell. This allows to measure mass changes under high pressures and at high temperatures. The measuring force is transmitted without contact, from a permanent magnet to the electromagnet connected to the balance. The polymer sample is filled in a transparent container attached by a suspension rig to the permanent magnet. The density of the surrounding atmosphere can be measured by means of a sinker with defined weight and volume. The software MessPro (Rubotherm, Bochum) provides a graphic presentation of the mass changes in the sample by absorbed gas depending on the time. Diffusion coefficients of carbon dioxide in the polymer melt were determined by measuring weight changes of the polymer during the sorption process. The calculations were accomplished by the equation of Crank and Park (1) for one-dimensional, one-sided diffusion. The determined diffusion coefficients remain constant during the sorption process. The measurements start in vacuum and last until the saturation is reached at a certain pressure. M_0, M_t and M_∞ are respectively the weights of the sample at the beginning of the sorption process, at any given time t, and at phase equilibrium, when the saturation process of the polymer with the gas is completed. In equation (2) H presents the height of the pure molten polymer layer in the container in vacuum, which can be calculated by using the pictures of the sample in the view cell.

$$1 - G = \frac{M_\infty - M_t}{M_\infty - M_0} = \frac{8}{p^2} \sum \frac{1}{(2n-1)^2} \exp\left[-\left(\frac{p}{2}\right)^2 (2n-1)^2 Fo\right] \tag{1}$$

$$D = \frac{Fo\, H^2}{t} \tag{2}$$

RESULTS AND DISCUSSION

Melting behavior

PEG 6000 [5] melts at ambient pressure at 60°C. **Figure 6** shows the melting behavior of pure PEG 6000 and of the polymer saturated with carbon dioxide. The curve represents a three phase (s-l-g) equilibrium curve. The solved gas causes a slight rise in the melting temperature at pressures between 5 and 10 bar. At low pressures a small amount of carbon dioxide (about 1%) is dissolved in the polymer. The slight increase at low pressures could be caused by the temperature increasing effect of static pressure on the melting temperature of pure substances, which outweighs the dimishing effect of dissolution of gas in the melt. Alternatively solid-solid transitions in the PEG´s could cause a rise in melting temperature. Increasing the pressure to 90 bar results in rapid decrease of the melting temperature. At pressures above 90 bar the melting temperature remains nearly constant with increasing pressure. In Figure 7 similar runs show the melting curves of the binary systems PEG 4000-CO_2 [6], PEG 12000-CO_2 [7] and PEG 35000-CO_2 [6]. The melting point decreases with increasing carbon dioxide concentration in the polymer, and reaches a minimum. Further rise in pressure doesn't change the melting temperature with the exception of the system PEG 35000-CO_2.
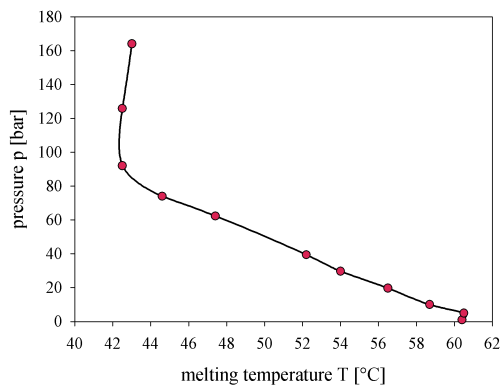
**Figure 6**: s-l-g equilibrium curve of the binary system PEG 6000-CO_2
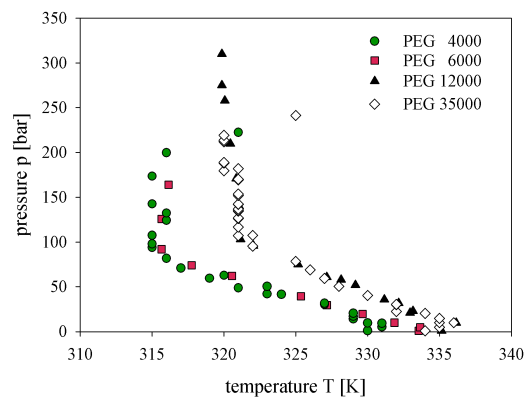
Figure 7: s-l-g equilibrium curves of various binary PEG-CO_2 systems

Solubility and dynamic viscosity

Figure 8 shows the compositions of the coexisting phases of the mixture PEG 6000-carbon dioxide at 80, 100 and 120°C. The curves on the left side show the isothermal determined compositions of the gas-rich polymeric liquids. As a maximum 27 percent CO_2 at pressures higher than 300 bar are dissolved in the melts. The measured

compositions of the CO$_2$-rich phases are presented on the right side of the graph. The quantity of solved polyethylene glycol in carbon dioxide amounts less than 2 percent and is within the accuracy range of the applied measuring method. With increasing pressure and decreasing temperature more carbon dioxide is dissolved in PEG 6000.
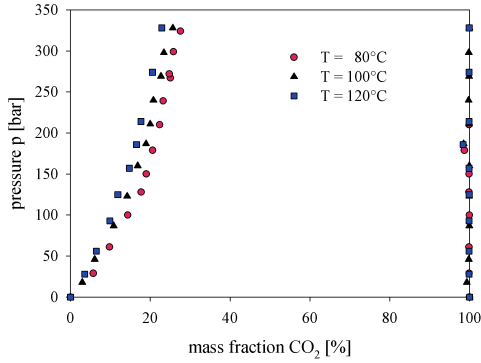

**Figure 8**: Compositions of the coexisting phases of the system PEG 6000-CO$_2$
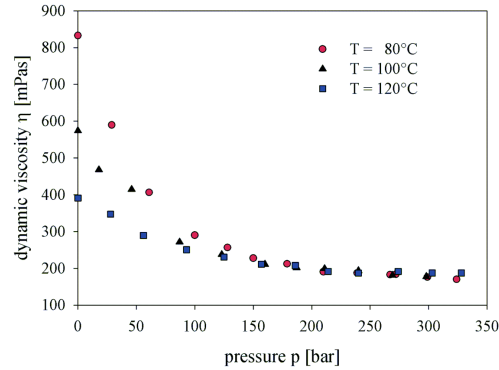
Figure 9: Dynamic viscosities of the pure PEG 6000 and gas saturated PEG 6000

The dynamic viscosities of the binary mixture PEG 6000-CO$_2$ at 80, 100 and 120°C depending on carbon dioxide-pressure are shown in **Figure 9**. The rise in the pressure, respectively the increased CO$_2$-solubility in the polymer melt, causes a drop in the dynamic viscosity of the melt. As an example this is shown for T = 80°C and p = 50 bar (see circles). The viscosity of the melt, which contains 8 percent, dissolved CO$_2$, declines to 40 percent, referring to the dynamic viscosity of the pure polymer at the same temperature at ambient pressure. At pressures higher than 150 bar nearly no further decrease of the viscosity is observed. The effect of the temperature on the dynamic viscosity is almost negligible at high pressures. The viscosities approach a constant value; though one should consider the occurring opposite effect of the temperature. An increase in the temperature causes a decrease in the viscosity, and furthermore in the solubility of the gas in the polymer melts. At 80°C and pressures higher than 250 bar, the viscosities have lower values than those at 120°C. The higher solubility due to lower temperature prevails over the increasing viscosity at reduced temperature. A drop in the viscosity by 75 percent was observed at pressures above 300 bar. The combined consideration of the pressure-composition- and the pressure-dynamic viscosity-relationship gives an indication of how much carbon dioxide needs to be added to the process in order to reduce the melt viscosity by a certain ratio.

The solubility of carbon dioxide in PEG 6000 and the diffusion coefficients of carbon dioxide in the polymeric melt have been measured additionally by the in situ gravimetric method in the magnetic suspension balance. The compositions of the gas saturated melts, obtained by both methods: sampling out of the autoclave and in situ gravimetric measurements, are shown in **Figure 10**. The results show a satisfying agreement. **Figure 11** shows the diffusion coefficients of carbon dioxide in liquid PEG 6000 determined by gravimetric measurements depending on time at 62°C and 80°C and at pressures up to 350 bar. A rise in the temperature leads to higher diffusion coefficients. With increasing pressure the values of the diffusion coefficients decrease.
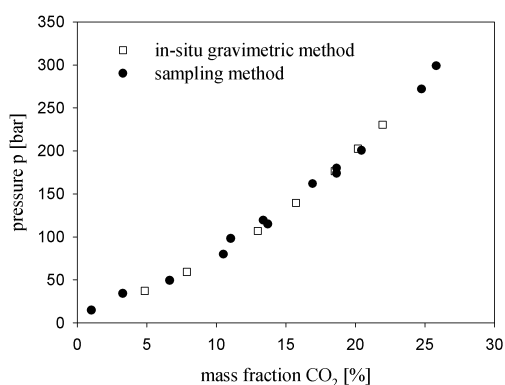
Figure 10: Solubilities of CO_2 in PEG 6000 by two various methods
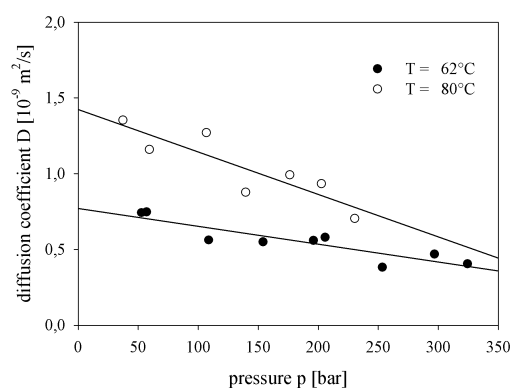
Figure 11: Diffusion coefficients of CO_2 in PEG 6000

CONCLUSIONS

The solubility of carbon dioxide in polyethylene glycols was determined for a range of pressures between 1 and 350 bar and temperatures from 80 to 120°C. The measurements were performed with the sampling method in an autoclave and in situ gravimetric method in a magnetic suspension balance. The first method is suitable for measuring solubilities of gases in polymer melts of low viscosity. For high viscous substances (viscosity > 10 Pas) the in situ gravimetric method should be applied. Detailed information about the application fields of both methods, gives [7]. The measurements are characterized by increasing solubility of carbon dioxide in PEG for each temperature with the increase of the pressure. On the other hand the solubility increases with the decrease of the temperature. The melting behavior of various PEG-CO_2 systems was determined in a high pressure view cell. The dissolved gas causes a decrease in the melting point of the binary systems of up to 13 K. Furthermore the viscosity and the diffusion coefficients of the PEG 6000-CO_2 mixtures have been measured. The viscosity decreases with increasing temperature and pressure. The dissolved gas reduces the viscosity of the polymer melts by 75 percent. The diffusion coefficients decrease with increasing pressure and increase with rising temperature. Nevertheless, the diffusion coefficients depend weakly on the concentration of dissolved gas.

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