

HIGH PRESSURE PHASE BEHAVIOR OF CO₂ AND POLYDIMETHYLSILOXANES

Stefanie Lang*¹, Marta Pérez², Sabine Kareth¹, Eckhard Weidner¹

¹Institute of Thermo- and Fluid Dynamics, Processes Technology; Ruhr-University Bochum, 44780 Bochum, Germany, ²Department of Chemical Engineering and Environmental Technology; University of Valladolid, 47005 Valladolid, Spain

Email: lang@vtp.rub.de, Phone : +49 234 32 26443, Fax: +49 234 32 14277

High pressure impregnation using dense gases as a carrier fluid is a promising technique to modify substrates and enhance their properties. The basis for a successful process design is certain knowledge about the impregnant's phase behaviour with the carrier fluid. There is a multitude of substances that come into consideration as impregnant agents. Hence, a time-saving method is needed to allow broad screenings of possible substances.

In this work, polydimethylsiloxanes of three different molecular weights were chosen as model impregnants because of their hydrophobizing properties. Carbon dioxide was applied as the carrier fluid due to its good solvent quality for non-polar substances. Solubility measurements have been carried out at 25, 40 and 60 °C and at pressures up to 30 MPa according to the static-analytic method and by the determination of cloud point pressures. It was found that both methods' results are in good agreement and that the latter method consumes considerably less experimental time. Sample solubility data was correlated satisfactorily with the PC-SAFT equation of state.

INTRODUCTION

Conventional impregnation processes are a versatile technique to hydrophobize substrates, improve their mechanical properties or impede the flammability. Recently, new impregnation processes have been developed applying dense gases or supercritical fluids because of their ability to penetrate deep into porous materials and to swell polymers. Examples are the preparation of controlled drug release systems [1, 2, 3], the fungicidal treatment of wood [4, 5], supercritical polymer blending [6] and the dyeing of natural or polymeric fibres and textiles [7, 8, 9].

As for most processes, knowledge about the phase behavior of the involved substances is essential for successful future applications. It is of interest to screen various possible impregnants with manageable experimental effort and time. A common and relatively quick approach for measuring solubilities in multicomponent or pseudo-binary mixtures is the determination of cloud point curves [10]. In this work, polydimethylsiloxanes (PDMS) are chosen as model impregnants to investigate the performance of the cloud point method compared to the determination of phase equilibria with the static-analytic method. PDMS exhibit a strong hydrophobizing effect and are thus possibly applicable as water-repellent agents using a supercritical impregnation process. Three different PDMS with a molecular weight of 4800, 11000 and 18000 g/mol have been applied in this work. Carbon dioxide is used as solvent because of its good miscibility with non-polar substances.

The high pressure phase behaviour of CO₂ and PDMS covering a molecular weight range from 38600 to 369200 g/mol has already been investigated by other authors using cloud point techniques [11, 12, 13]. To the author's best knowledge, solubility data of relatively low molecular PDMS over the complete range of concentrations is not available nor has the static-analytic method been applied to these systems. Alessi et al. provide data on the solubility of low viscous PDMS with unknown exact molecular weight in CO₂ for the light phase at 40 and 60 °C [14]. O'Neill et al. determined cloud point pressures of mixtures containing up to 17.3 wt% PDMS (M_w = 13000 g/mol) [15].

With the present work this gap in solubility data is closed as high pressure phase equilibria of CO₂ and the above mentioned three different PDMS have been investigated at 25, 40 and 60 °C and at pressures up to 30 MPa. Furthermore, cloud point curves were determined at the same isothermal conditions. The obtained solubilities in the dense phase are in very good agreement with the former method which is considered as a reference technique.

Lastly, sample solubility data has been modelled applying the PC-SAFT equation of state. The experimental values were correlated satisfactorily using pure substance parameters from the literature.

MATERIALS AND METHODS

Materials. Three different commercially available polydimethylsiloxanes were obtained from Wacker (Munich/Burghausen, Germany). For our studies the samples were used as received. Gel permeation chromatography with toluene as solvent was performed to determine both the molecular weight and the polydispersity. The analytic system was a Viscotek GPCmax equipped with a TDA 305 triple detector (refractive index, light scattering and viscosity). Absolute molecular weights were calculated by applying the typical value of -0.89 ml/g of the refractive index increment dn/dc for PDMS in toluene. The results and further properties of the samples are collected in table 1.

Table 1. Data of the applied polydimethylsiloxanes

Viscosity (mm ² /s)	Mw (g/mol)	PD
50	4800	1.4
150	11000	1.8
350	18000	2.0

Carbon dioxide was obtained from Yara Industrial (Dülmen, Germany) with a purity of 99.9 % v/v. It was dried using zeolites to reduce the water content to approximately 5 ppm v/v.

Apparatus. A cylindrical high pressure view cell with a stirrer was used for all solubility experiments. The cell was heated electrically with heating rods and the temperature was kept constant within ± 1 °C using a PID controller. Pressure and temperature were measured with a transducer and a type K thermocouple, respectively. A hydraulic piston allows varying the volume of the cell in the limits between 24 and 57 ml.

Static-analytic method. High pressure phase equilibria of the three PDMS-CO₂ systems have been determined according to the static-analytic method at 25, 40 and 60 °C. Therefore, the cell is purged with CO₂ and charged with PDMS before the experiment. Afterwards, CO₂ is pumped into the apparatus to the desired pressure. The mixture is stirred and then equilibrated. Samples were drawn both from the light and the dense phase in equilibrium

state. During the sampling procedure the pressure was held constant by changing the cell's inner volume with the hydraulic piston. The samples were analyzed gravimetrically before and after degassing at ambient pressure. A gas flow meter was used to measure the volume of CO₂ that demixed instantly from the sample stream. The corresponding mass was calculated with densities obtained from an equation of state for carbon dioxide developed by Span and Wagner [16].

Cloud point method. The equipment is prepared and charged with PDMS as described above. Then, CO₂ is pumped into the cell until single phase conditions are reached. A sample is drawn according to the above procedure to determine the system's composition. Afterwards, the pressure is reduced at a constant temperature and composition with the hydraulic piston. The cloud point is then observed visually through the sapphire windows. During the procedure the system is well stirred. After demixing, the pressure was increased again to single phase conditions and the procedure was repeated another two times for every measurement point.

It is reported that the visual method is in good agreement with the photoelectrical determination of cloud point transitions for polymers with a polydispersity of less than 3.0 [10]. Generally, the pressure range of the cloud point transition was below 0.1 MPa to 0.2 MPa. For CO₂ contents of less than 15 wt% and for compositions close to the upper critical solution pressure the range is typically enlarged to 0.5 MPa. In one case, an extreme range of up to 1.7 MPa was observed for a mixture containing 14.9 wt% of the low molecular weight PDMS ($M_w = 4800$ g/mol) at 40 °C. Concerning the appearance of the transition, low demixing pressures and high polymer contents lead to a turbid and turbulent veil. At high demixing pressures and accordingly low polymer contents, the cloud point occurs as an instantaneous, sharp darkening. Samples are given in the following figures.

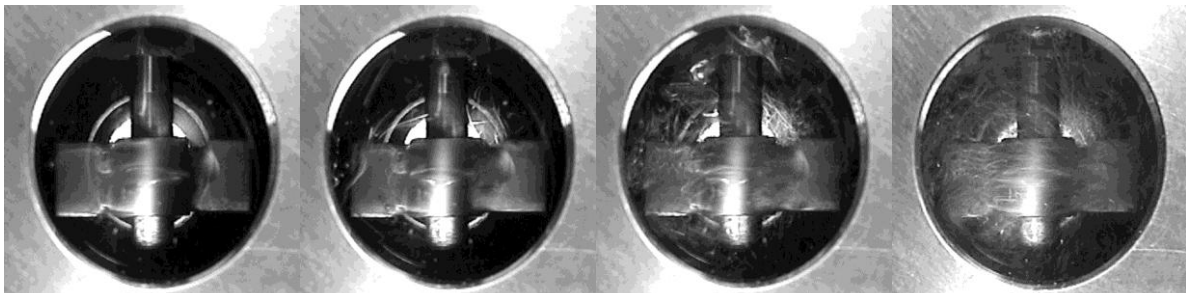


Figure 1. Transition of a mixture containing 90.0 wt% PDMS ($M_w = 11000$ g/mol) at 60 °C. The pictures correspond to pressures of 6.5 (still one phase condition), 6.2 , 6.1 and 5.9 MPa.

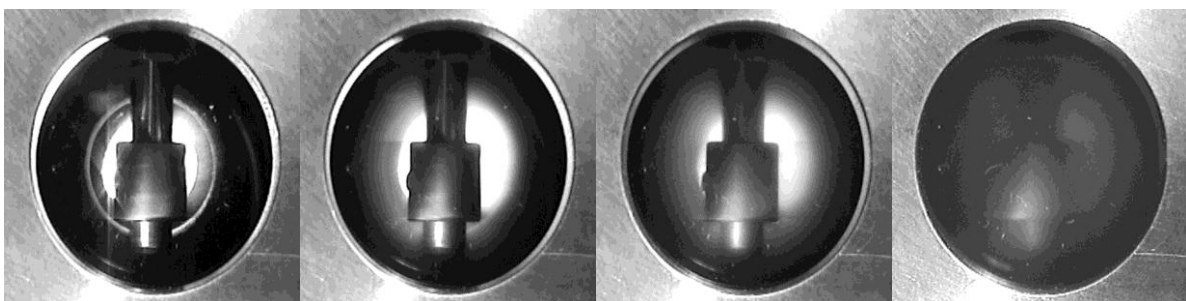


Figure 2. Transition of a mixture containing 53.9 wt% PDMS ($M_w = 11000$ g/mol) at 60 °C. The first picture corresponds to a single phase condition at a pressure of 18.2 MPa while the following pictures present the complete development of the transition at 18.1 MPa.

EXPERIMENTAL RESULTS

Regarding the phase behavior, it was found that the systems exhibit a better mutual solubility with increasing pressure as well as with a decrease in temperature and molecular weight of the PDMS. A high degree of reproducibility was achieved with both, the static-analytic and the cloud point method. Furthermore, the methods' results agree very well for the dense phase (Figure 3).

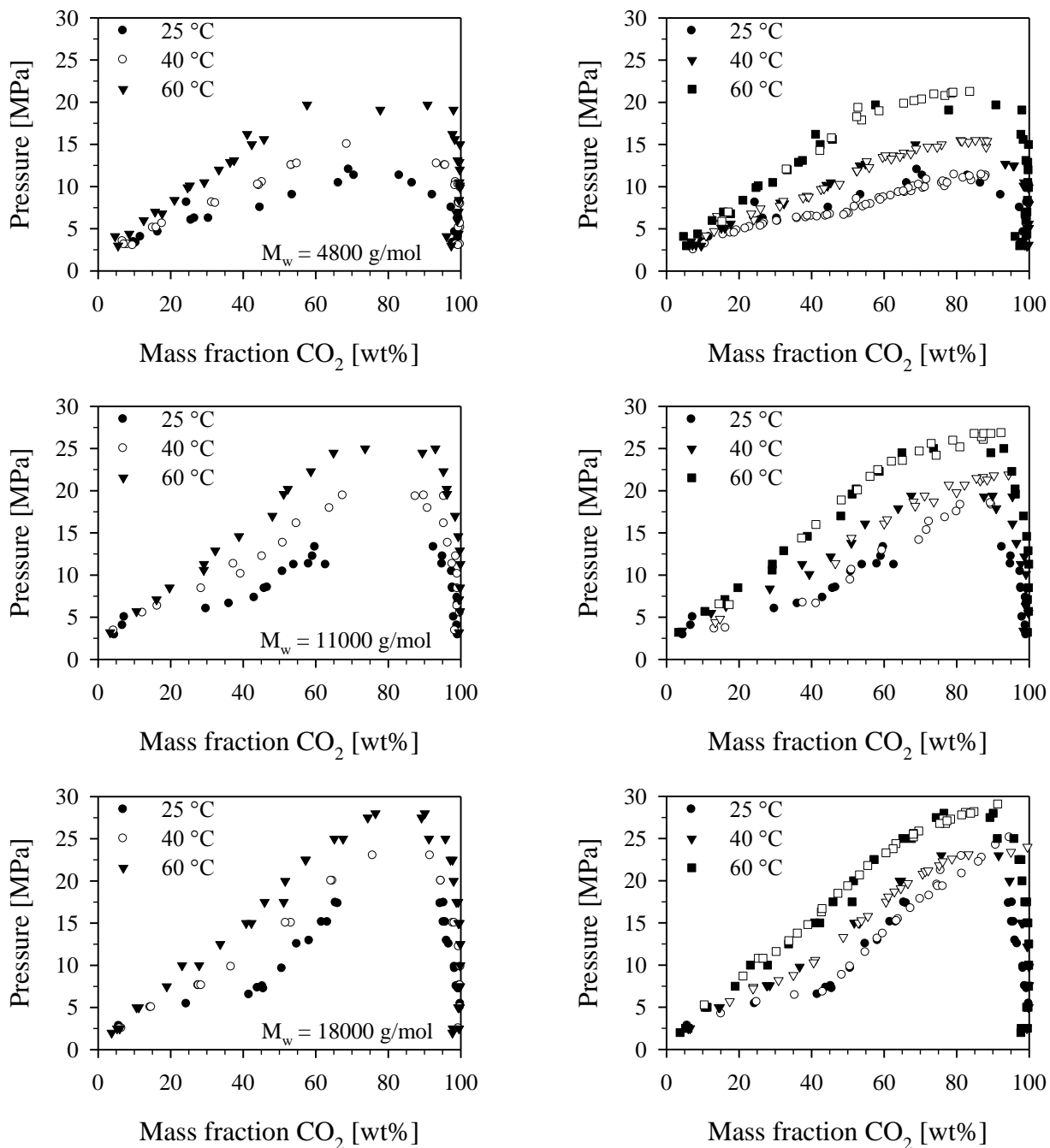


Figure 3. Experimental solubilities for mixtures of PDMS and CO₂. Left pictures show the results of the static-analytic method, right pictures compare this data (closed symbols) to the cloud point method (open symbols).

The present results show that the static-analytic method can be replaced by means of the suggested cloud point method for the investigated systems if data of the dense phase has to be obtained. For the light phase, the cloud point demixing pressures deviate from the equilibrium data. Nevertheless, this change is recognized during the experiment by the cloud points' augmenting pressure transition range.

Applying the cloud point procedure is advantageous as in contrast to the static-analytic method no equilibration of the system is needed. The equilibration takes a time of up to one hour or more at high pressures. Consequently, one complete cloud point curve is determined within one day while in the same time only three or four equilibrium measurements can be conducted.

THERMODYNAMIC MODELLING

The Statistical Associating Fluid Theory [17] with the Perturbed-Chain modification (PC-SAFT) [18] was used to model the obtained solubility data of CO₂ in the middle molecular weight PDMS (M_w = 11000 g/mol). The model describes molecules as chains composed of spherical segments and is expressed in terms of the residual Helmholtz free energy a^{res} . For non-associating fluids this energy can be calculated as the sum of the hard-chain repulsive forces a^{hc} and the contribution due to dispersion forces [17].

$$a^{res} = a^{hc} + a^{disp} \quad (1)$$

Three parameters are used to describe the mixtures. The number of segments in a polymer chain is represented by the parameter m , σ is the segment diameter and ε is the depth of the pair potential. The following table summarizes the pure substance parameters that were used in this work.

Table 2. Applied PC-SAFT pure substance parameters

Substance	m (-)	σ (Å)	ε/k (K)	Reference
CO ₂	2.0729	2.7852	169.21	[18]
PDMS	0.03252·M _w	3.5321	205.32	[19]

Conventional Berthelot-Lorentz mixing rules are applied to calculate the mixtures' parameters with k_{ij} as single binary interaction parameter [18].

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (2)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} (1 - k_{ij}) \quad (3)$$

The binary interaction parameter k_{ij} has been fitted by minimizing the absolute average deviation (AAD) (equation 4) between calculated bubble point pressures and pressure values of the static-analytic phase equilibrium experiments (Table 3).

$$AAD = \frac{1}{n} \sum_{i=1}^n \frac{|Y^{\exp} - Y^{calc}|}{Y^{\exp}} \cdot 100 \quad (4)$$

Table 3. Experimental solubilities of CO₂ in PDMS (M_w = 11000 g/mol)

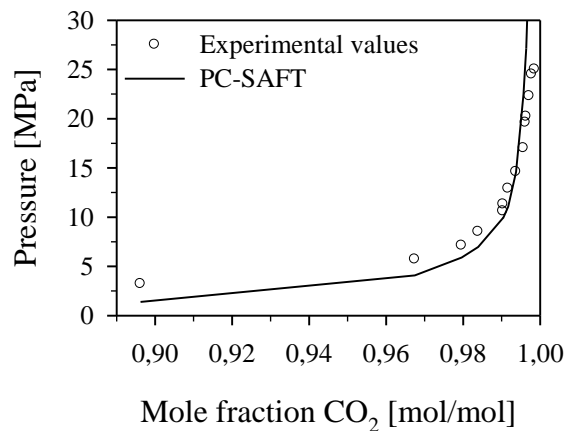
T = 25 °C		T = 40 °C		T = 60 °C	
P (MPa)	w _{1,CO2} (wt%)	P (MPa)	w _{1,CO2} (wt%)	P (MPa)	w _{1,CO2} (wt%)
2.9	4.6	3.4	4.3	3.2	3,3
4.0	6.8	5.5	12.3	5.7	10.6
5.0	7.3	6.3	16.4	7.1	16.1
6.0	29.8	8.4	28.5	8.5	19.7
6.6	36.2	10.1	39.4	10.6	29.1
7.3	43.1	11.3	37.4	11.3	29.2
8.4	45.9	12.2	45.3	12.9	32.3
8.5	46.7	13.8	51.0	14.6	38.8
10.4	50.9	16.1	54.8	17.0	48.1
11.2	54.0	17.9	63.9	19.6	51.2
11.3	58.1	19.3	87.5	20.2	52.3
12.2	59.2	19.4	67.5	22.3	58.6
13.3	59.8				

The calculated solubilities correlate satisfactorily the experimental data with an ADD < 1.3 %. The obtained best fit results are summarized in Table 4.

Table 4. PC-SAFT binary interaction parameters and associated average absolute deviation

T (°C)	k _{ij} (-)	AAD (%)
25	0.0628	1.3
40	0.0540	0.8
60	0.0620	0.6

The pure component parameters for PDMS from the literature [19] were fitted to pseudo experimental PVT data computed with the Tait equation [20]. It is not clear which pressure and temperature intervals were selected for the parameter fit, which might be a reason for the deviations occurring in the present correlation. A sample diagram with a comparison between experimental and calculated data is given in Figure 4.

**Figure 4.** Solubility of CO₂ in PDMS (M_w = 11000 g/mol) at 60 °C

CONCLUSION

This study has shown that for the investigated PDMS-CO₂ mixtures both, the static-analytic method and the cloud point method deliver the same solubility data for the dense phase. This is not self-evident as for all polymer solutions fractionation effects can be of a concern. For the sake of experimental effort, the use of the cloud point method is recommended. Nevertheless, for new systems it is advisable to check the results by determining few static-analytic measurement points. Special care should be taken if polymers with a large polydispersity are applied.

The PC-SAFT equation of state was applied successfully to the experimental data using pure component parameters from the literature allowing the interpolation of data.

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