



## Phase equilibria in process design for the production of polymers derived from carbon dioxide



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### ABSTRACT

The optimisation of an innovative process where carbon dioxide (CO<sub>2</sub>) is used as raw material for the production of polyurethane precursors relies strongly on the physical properties and phase equilibria of the mixtures involved. In this work, we present experimental results for high-pressure phase equilibria of systems involving CO<sub>2</sub>, propylene oxide, different polyether carbonate polyols (CO<sub>2</sub>-PET) and propylene carbonate, at pressures up to 8 MPa and temperatures between 373 K and 393 K. Low-pressure phase equilibria were determined for the system CO<sub>2</sub>-PET + propylene carbonate, at temperatures between 373 K and 414 K, at pressures below 30 hPa. Furthermore, the solubility of nitrogen in CO<sub>2</sub>-PET was determined at room temperature at pressures up to 0.5 MPa. Different apparatus were employed in this work, based on synthetic methods.

The high-pressure experimental results were modelled with the Soave–Redlich–Kwong equation of state, with the Pénélox–Rauzy volume translation and Mathias–Klotz–Prausnitz mixing rules. The ability of the method to predict multicomponent phase equilibria using parameters fitted to binary data only was tested. Low-pressure results were modelled using the Non-Random Two Liquid (NRTL) model.

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### 1. Introduction

The targets for the reduction of greenhouse gas emissions and of energy consumption in the chemical industry were set high, with companies investing in ambitious environmental programs which often require the development of innovative products and processes. One option to improve the carbon footprint and sustainability is to use CO<sub>2</sub> as a substitute for fossil feedstock. In the polymer industry, CO<sub>2</sub> can be integrated into the molecular structure of polymers, reducing the dependence of the process on crude oil derivatives on one hand, and providing an application for the CO<sub>2</sub> originated from fossil-fuel combustion in power plants. In this framework, the potential of the catalytic copolymerisation of epoxides and CO<sub>2</sub> to polycarbonates becomes prominent, as polyether polyols normally used in the preparation of foams, adhesives, coatings and fibres, representing a multi-million ton per annum industry, can be substituted by tailored polyether carbonate polyols

[1]. An additional advantage is the high durability of the new CO<sub>2</sub>-based materials [1].

A pilot plant was already built and successfully produces polymer of high quality, with an incorporation of CO<sub>2</sub> above 20 wt% [2]. The challenge is now to find the best production parameters. Many upstream aspects, which include the choice of the catalyst, reaction conditions, etc., have been the focus of several publications [1–5]. Apart from these, also the distribution of the various species between the different phases is crucial for a complete description and modelling of the reaction process. Furthermore, phase equilibria are particularly crucial in the selection and optimisation of the separation processes for the downstream part of the process, where the product needs to be purified in order to meet specifications.

In parallel with the experiments in the pilot plant, the complete process was implemented in a process simulator, describing the reaction and chemical composition under different conditions and equipment, and allowing the optimisation of the subsequent separation processes. If available, information on the phase equilibria was taken from literature, otherwise experimental determination was required. Combining simulation and experiments, recipes and conditions are improved, resulting in an evolution of the reaction process, leading to products of different characteristics. In a

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previous work, we have already presented data for the solubility of CO<sub>2</sub> and of propylene oxide (PO) in the polyol [6], but new measurements are required as the process and the final product evolve towards their optimal.

Information on phase equilibria was found in literature for the systems PO + CO<sub>2</sub> [7–9], and propylene carbonate (PC) + CO<sub>2</sub> [10–17]. The solubilities of CO<sub>2</sub> and of PO in pure polyether carbonate polyol (CO<sub>2</sub>-PET), and in mixtures of CO<sub>2</sub>-PET with PC were determined experimentally. Results include the study of the solubility of gas mixtures, for the ternary system CO<sub>2</sub> + PO + CO<sub>2</sub>-PET and for the quaternary system CO<sub>2</sub> + PO + CO<sub>2</sub>-PET + PC, allowing a better assessment of the influence of PO on the solubility of CO<sub>2</sub>, an aspect not considered in the previous measurements [6]. Experiments were performed in the temperature range between 373 K and 393 K, at pressures up to 8 MPa for the CO<sub>2</sub> solubility measurements, and up to 0.6 MPa for the determinations of the PO solubility.

In the framework of risk assessment studies, the solubility of nitrogen was also considered. Literature values were found for the solubility in PC [12,18], and in PO [19]. The solubilities of N<sub>2</sub> in CO<sub>2</sub>-PET were determined experimentally at room temperature and at moderate pressures, up to 0.5 MPa. The equilibrium between water and PC was also taken into account, with values retrieved from literature [20,21].

Finally, the low-pressure phase equilibrium for the system PC + CO<sub>2</sub>-PET was measured between 373 K and 413 K, at pressures below 30 hPa, for application to the downstream part of the process.

The experimental high-pressure results obtained for the binary systems, i.e., solubilities in pure CO<sub>2</sub>-PET, were modelled using the Soave–Redlich–Kwong (SRK) model implemented in the Aspen 7.2 simulator (AspenTech, USA) [22]. This model uses the SRK equation of state [23] with the volume translation concept introduced by Pénélox and Rauzy [24], and the Mathias–Klotz–Prausnitz (MKP) mixing rules [25]. The low-pressure results were modelled using the Non-Random Two Liquid (NRTL) activity coefficient model [26], also implemented in the same simulator [22].

## 2. Experimental

### 2.1. Chemicals

For the experimental determinations, two different samples of CO<sub>2</sub>-PET were used in the measurements, from now on denominated CO<sub>2</sub>-PET-A and CO<sub>2</sub>-PET-B. CO<sub>2</sub>-PET-A had an overall mass fraction CO<sub>2</sub> content of 0.208 and a hydroxyl number of 55.3, with a calculated molecular weight of 3043 g mol<sup>-1</sup> and a polydispersity index (PDI) of 1.10.

As for CO<sub>2</sub>-PET-B, the polyol had an overall mass fraction CO<sub>2</sub> content of 0.215 and a hydroxyl number of 48.2, with a calculated molecular weight of 3282 g mol<sup>-1</sup> and a polydispersity index (PDI) of 1.09.

The commercial substances CO<sub>2</sub> and N<sub>2</sub> were obtained from Linde AG with a mass fraction purity of 0.99995 and 0.99999 respectively, while PO was supplied by J. T. Baker with a mass fraction purity superior to 0.99. Propylene carbonate was obtained from Sigma–Aldrich, having a mass fraction purity of 0.999.

### 2.2. Experimental method

All measurements were performed using synthetic methods, which avoid any type of sampling [27–29]. The synthetic-isothermal method, particularly suitable for determinations of solubilities of a gas in non-volatile condensed phases, was used in most experiments, similarly to the procedure already described in a

previous work [6]. The method, its advantages and disadvantages have been described in great detail elsewhere [27–29]. Attention was given to experimental details so as to maximise the quality of the results [30].

High-pressure measurements were performed in a view-cell, which enables the visual determination of the volumes of both phases in equilibrium. The high-pressure cell is made of Hastelloy C4 and equipped with sapphire windows. It has an internal volume of 250 cm<sup>3</sup> and it is suitable for pressures up to 35 MPa. A more detailed description of this apparatus can be found in the literature [31].

The low-pressure experiments were performed following a similar procedure, using a glass cell with an internal volume of 350 cm<sup>3</sup>. This cell consists of a glass cylinder placed between two stainless steel flanges. The temperature is measured using a Pt100 resistance thermometer (calibrated with a triple-point cell and against thermometers calibrated at DKD Deutscher Kalibrierdienst) accurate to within ±0.1 K, and the pressure is monitored through a high-precision pressure transducer Keller PAA-33X (Keller AG, Switzerland) with a range of 0.1 MPa. The transducer was calibrated before each experiment for a specific temperature and for the entire relevant pressure range using a pressure balance calibrated in regular intervals at Europascal GmbH, accredited by DKD Deutscher Kalibrierdienst. The pressure transducer and the thermometer are connected to a computer for monitoring and recording of the data.

For the experiments involving gas mixtures (CO<sub>2</sub> + PO), a synthetic method with phase transition [27–29] was used. In this method, a mixture of exact composition is first added to the equilibrium cell, and the conditions (most commonly the pressure) are altered leading to the disappearance of one of the existing phases or the appearance of a new phase. In this particular work, the previously evacuated cell was first loaded with the condensed phase (pure CO<sub>2</sub>-PET or CO<sub>2</sub>-PET + PC), followed by a well-determined amount of PO, and finally CO<sub>2</sub>. Once the temperature was stable, the pressure was increased stepwise, by varying the volume of the cell. For every step, the volume and the pressure in equilibrium were recorded. The procedure was repeated until only one phase was present. This was detected by a strong variation in the *pV* slope, given the reduced compressibility of the system when no gas phase is present, as illustrated in Fig. 1 [28]. It is advisable to repeat the experiment reducing the pressure stepwise in order to detect the reappearance of the gas phase. Hysteresis can be a symptom of a poor equilibrium at each step of the experiment, meaning that longer waiting times are necessary. After one determination, more CO<sub>2</sub> was added to the cell for a new global composition, and the procedure was repeated. The method has been described in detail elsewhere [27–29] and its advantages and disadvantages discussed.

The measurements based on the synthetic method with phase transition were performed in the high-pressure view-cell described above, after substituting one of the sapphire windows with a bellows, which allows varying the volume of the cell.

## 3. Results

### 3.1. Solubility of CO<sub>2</sub> in CO<sub>2</sub>-PET and PC

The solubility of CO<sub>2</sub> in pure CO<sub>2</sub>-PET-A was determined at two temperatures, 373 K and 393 K, at pressures up to around 8 MPa. The results are shown in Table 1 and in Fig. 2, where the curves correspond to the modelling of the results using the SRK equation of state. The plot shows a linear increase of the CO<sub>2</sub> solubility with pressure. The model gives a reasonably good approximation of the experimental results. When comparing the current results with

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