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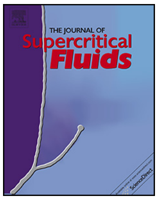

Thermodynamic data for processing polyethylene glycol with non-conventional fluids

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ABSTRACT

Melting points of polyethylene glycols (PEGs) with molar masses (1500, 4000, 10 000 and 35 000) g/mol under pressure of propane and sulfur hexafluoride have been determined and were compared with previous published data with CO_2 and argon. Additionally, solubilities of argon and CO_2 in PEGs have been determined along the melting curve. The desorption of gases from PEG to constant mass at atmospheric conditions was followed for propane, CO_2, argon and SF_6–previously the system was exposed to conditions 343 K and 15 MPa. Finally, PGSS micronization of PEG with molar mass 1500 g/mol with fluids propane, CO_2, argon and SF_6 was successfully performed at two operating conditions: at the minimal melting point of PEG under fluid and at 328 K and 15 MPa. This is the first report of PEG micronization with unconventional fluids: propane, SF_6 and argon.

1. Introduction

Changing the physical properties of solid materials is an important issue in different chemical industries. The size, morphology and particle size distribution of the material are important for consumers – normally they demand specific characteristics of the material they are purchasing.

Reducing the size of the solid particles is conventionally done with mills or by applying hazardous organic compounds, which may harm the material or remains of organic compounds stay in the material, which is unacceptable in the food or pharmaceutic industry and medicine. Therefore supercritical fluids represent an alternative to those conventional micronization methods, with almost no impact on the processed material or on the environment – depending on the fluid used [1].

Processing polymers with supercritical fluids is an interesting field in the polymer industry [2] and knowledge of high-pressure equilibria, diffusivity etc. for establishing such processes is essential [2–4]. Carbon dioxide is the mostly used supercritical fluid for polymer processing, but there are also other nonconventional fluids, which can have high potentials [5]. Different supercritical fluids have different impacts on the polymer, depending on the properties of the supercritical fluid; this can result in different particle size, morphology or particle size distribution [5].

One of the most often used polymers is polyethylene glycol (PEG), which is a water soluble polymer, physiological acceptable and biocompatible. It is often used in pharmaceutical, cosmetic and food industry [2,6]. Therefore we investigated the thermodynamic and transport data (melting point, solubility, desorption, diffusion coefficient) of the system polyethylene glycol/supercritical fluid with the following fluids: propane and sulfur hexafluoride. The data obtained in present work were compared with the data for the systems of PEGs with carbon dioxide [7] and argon [5] obtained in our previous work. These properties were determined for the purposes of planning the batch micronization process PGSS (Particles from Gas Saturated Solutions) of PEG with the before mentioned fluids.

2. Materials

Polyethylene glycols (PEGs) with different molar masses in the form of flakes produced by MERCK were used; the number after the acronym PEG denotes the molar mass (g/mol):

- PEG 1500 (Cat. no. 8.07489)
- PEG 4000 (Cat. no. 8.07490)
- PEG 10 000 (Cat. no. 8.21881)
- PEG 35 000 (Cat. no. 8.18892)

The following fluids were used:

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- Carbon dioxide (CO_2), 4.5, Messer, Slovenija
- Argon (Ar), 4.6, Messer, Slovenia
- Propane, 2.5, Linde plin, Celje, Slovenia
- Sulfur Hexafluoride (SF_6), 4.7, Istrabenz Koper, Slovenia

3. Methods

3.1. Determination of melting points

For the melting point determination by a glass capillary method glass capillary with length of 75 mm (Euroglass, Ljubljana, Slovenia) was used. A detailed description can be found in literature [5,8].

In the present article the melting points of PEG with molar mass 1500 g/mol, 4000 g/mol, 10 000 g/mol and 35 000 g/mol were determined under pressure of propane and sulfur hexafluoride up to pressure of 30 MPa.

PEGs were in a form of white flakes, therefore the PEGs were powdered with the PGSS micronization process using CO_2, so that the glass capillary could be filled. The micronization conditions were for PEG 1500: 313 K and 15 MPa, for PEG 4000: 324 K and 15 MPa, for PEG 10 000: 336 K and 13 MPa and for PEG 35 000: 344 K and 14 MPa, like reported in our previous article [5].

3.2. Determination of solubility and diffusion coefficient

3.2.1. Magnetic suspension balance

3.2.1.1. Solubility. A description of the magnetic suspension balance and the method for solubility determination is given in literature [5,7]. The Rubotherm magnetic suspension balance was used to determine the solubility of argon in PEG with molar masses 1500 g/mol, 4000 g/mol, 10 000 g/mol and 35 000 g/mol along the melting point curve of PEG under pressure of argon. Also the solubility of CO_2 in PEG with molar masses 1500 g/mol, 4000 g/mol and 10 000 g/mol along the melting curve of PEG under pressure of CO_2 was determined.

3.2.2. External balance method

3.2.2.1. Diffusion coefficients. The external balance method and the method for diffusion coefficient determination are described in literature [7]. The diffusion coefficients of propane, SF_6 and argon of the system PEG 1500/fluid were determined. The system was exposed to conditions of maximal pressure 30 MPa and temperature of 343 K.

3.2.2.2. Desorption. The time required for gas desorption from polymer at atmospheric conditions was determined for PEGs with molar masses 1500 g/mol, 10 000 g/mol and 35 000 g/mol for fluids propane, CO_2, SF_6 and argon. 0.5 g of PEG was placed in a glass sample container and in the autoclave. The system was heated to 343 K and pressurized up to 15 MPa. After equilibrium establishment (1 day) the system was depressurized to atmospheric conditions and the sample container with the sample as quickly as possible put on KERN 770 balance with accuracy ± 0.0001 g. The mass of the sample was recorded firstly in short periods of time (a few seconds), then half a minute, a minute (if the desorption was fast) till approximately 1 h (if the desorption lasted longer). Then the sample container with the sample was stored in a desiccators and after half an hour the sample was weighted again (this was repeated a few times). The sample was then weighted every day to obtain the period required to obtain constant mass of the sample.

After reaching equilibrium mass, the height of the sample in the container was measured with a calliper (Mitutoyo, 500-123U, CD-15B with accuracy 0.01 mm). We compared this height to the height of the unprocessed PEG. Because the unprocessed PEG was in form of flakes the sample for comparison was prepared in the following way: the same amount of sample was weighted in a sample container, heated at atmospheric conditions till melting point and cooled to room temperature.

3.3. Micronization by PGSS process

A description of a batch PGSS micronization is presented in literature [9]. A reactor (IPIM Zagreb, Croatia) with inner volume 130 mL, maximal operating pressure of 35 MPa and temperature 426 K was filled with PEG (20 g) and heated to the desired temperature with electric heater (METLER, Slovenia, HSN 260/10 M250). The reactor was equipped with temperature indicator (GTH 1150, Digital Thermometer NiCr-Ni) and pressure indicator (Nuova Fima EN837-1, 40 MPa). Then the fluid was introduced by a high-pressure pump (NWA PM-101) until the desired pressure was reached. After the established conditions, 1 h of mixing followed in order to establish equilibrium. The gas-saturated solution was then expanded through a nozzle with a diameter of 0.7 mm and spraying angle 60° into a spray tower. Two spraying towers with different dimensions were used.

3.4. Analysis of PGSS micronized particles

With scanning electron microscope (SEM) HR SEM, Helios Nanolab FEI 650 the morphology of the PGSS micronized PEG were analyzed. The samples were gold plasted with JEOL-JCF-1100 E Iou Sputler. The particle size was determined with the Cilas 1090 Laser Particle Size Analyzer – liquid mode (silicone oil).

4. Results and discussion

4.1. Melting points of polyethylene glycol under pressure of fluids

Melting points of PEGs with different molar masses were determined under pressure of propane and sulfur hexafluoride and are represented in Tables 1–4 (under Supplementary data) and Figs. 1–4 . The obtained data were compared to the data from our previous work for systems PEG/CO_2 [10] and PEG/argon [5].

Due to different nature of the used fluids they influence melting point of PEG under pressure of the fluid differently; it depends on the interactions between the fluid molecules and the polymer molecules.

Each fluid has its unique properties (molecule size, polarity, mobility etc.) and they also have a unique impact on the properties of PEG under pressure of fluids. Some properties of the used fluids are shown in Table 5 (Supplementary data).

Propane and sulfur hexafluoride (SF_6) molecules are much bigger than CO_2 molecules and the argon atom. For SF_6, which has the shape of an octaeder, it is difficult to move between the polymer chains. This is even more difficult for the linear propane molecule with the size of almost 5 A. Despite the big molecules, hindered movement and consequently decreased solubility of SF_6 and propane in PEGs compared to CO_2, decrease of melting point to a melting point minimum is observed under pressure of both gases – propane and SF_6.

The melting point minimum under argon occurs at 10 MPa (for PEGs of all molar masses) and under CO_2 between 10 MPa and 20 MPa. The melting point minimum under propane occurs between 4 MPa and 7 MPa and between 2 MPa and 4 MPa under pressure of SF_6.

All of the investigated systems show a melting point minimum (at higher pressures between 2 MPa and 7 MPa), where the solubility of the gas in the polymer is the highest, and a melting point maximum at lower pressures – between 0.2 MPa and 0.3 MPa, where the solubility of the gas in the polymer is the lowest. This cannot be seen in the graphs, but it is obvious from the data presented in the Tables 1–4 (under Supplementary data). The explanation of