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Solubility and binary diffusion coefficient of argon in polyethylene glycols of different molecular weights

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ABSTRACT

Thermodynamic data of polyethylene glycol in argon, based on a gravimetric method using a magnetic suspension balance are presented. Polyethylene glycol with an average molecular weight of 1500 (PEG 1500) and argon binary system was investigated at temperatures 343 K and from 373 to 433 K and pressures from 0 to 33 MPa with an increment of 2 MPa. Solubilities and diffusion coefficients of argon in polymer were also determined for PEG 4000, PEG 10000 and PEG 35 000 at a temperature of 373 K and pressures from 0 to 33 MPa. A comparison between solubility and diffusion coefficient for absorption and stripping process was made and the absorption rates were calculated. The melting points of PEG 1500, PEG 4000, PEG 10 000 and PEG 35 000 were determined by a simple glass capillary method. Results show that solubility is a strong function of temperature, pressure and gas density as it increases with increasing pressure at a constant temperature. Maximal solubility in the investigated range of conditions is approx. 0.05 g argon/g polymer at 373 K and 34 MPa. Diffusion coefficients increase with increasing temperature as a consequence of the increasing kinetic energy of the atoms and vary between 10^{-6} cm^2/s and 10^{-4} cm^2/s. Furthermore a 3% volume variation of PEG sample at temperatures above 373 K and 9% at 343 K could be observed. Molecular weight slightly influences the absorption rate of argon in PEG which is approximately 1.5×10^{-7} g/g s. The melting points in argon atmosphere are for approximately 20 K higher compared to those in CO_2 atmosphere.

1. Introduction

Supercritical fluid technologies are considered as green processes [1] and present an alternative to processes with harmful organic solvents [2] and also for processing of polymers.

Polymer processing with supercritical fluids (SCF) has been an interesting field of research over the last years and such high-pressure processes are widely used in the polymer industry [3]. With SCF polymer structures with different morphology and shapes (particles, fibres, foams) can be obtained for use in pharmaceutical, food and cosmetic industry, medicine, coating industry, etc. [4] In order to create such structures, it is important to study the binary systems of different polymers and SCF [1].

For designing and optimising processes of polymer processing using supercritical fluids, the knowledge of high-pressure equilibria, solubility, diffusivity, density and permeability is essential [3,5–7] and were intensively researched in the past years [8–16]. Polymer processing includes micronisation, encapsulation, foaming, impregnation, etc. Gas solubility and diffusivity data in the polymer are of a crucial importance in polymer foaming which is dependent on gas dissolution, bubble nucleation and growth [17]. The supercritical fluid has a unique impact on the processed polymer due to the specific properties of the polymer and the SCF. Parameters that affect the behaviour of the binary system polymer/SCF are the nature of the polymer (polymer state, crystallinity, crosslinking, chemical structure, glass transition temperature T_g), the SCF (molecular structure, the critical point, polarity of the gas molecule), the molecule interactions between polymer and SCF and the process conditions (temperature, pressure, depressurisation rate) [6,7]. With the knowledge of the physical and thermodynamic properties of the polymer/SCF system the behaviour of the system and the morphology and functionality of the processed polymer can be predicted [1].

Polyethylene glycols (PEGs) are taken in consideration because of their physiological acceptance and biocompatibility and are widely used in pharmaceutical, cosmetic and food industry [3,18]. According to literature review, mostly supercritical carbon dioxide (SC CO_2) is used for polymer/SCF system researches [1,3,4,6,8,10–14,18–21], but there are also other fluids, which are less known and have high potentials for industrial applications. In

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the present work, the behaviour of argon at supercritical conditions and its thermodynamic properties within a binary system with a polymer has been studied. No data were found for the polyethylene glycol/supercritical argon system.

Argon is one of the cheapest noble gases; it is chemically inert and it has no chemical impact on the substance, but it can easily modify the physical properties of the substance (viscosity, density, melting temperature, etc.) [2]. Argon has a critical temperature at 151 K and its critical pressure is at 4.863 MPa. Due to the complete eight electrons in the outer atomic shell of the atom, argon unreactivity probably does not change at supercritical conditions.

The melting points and the behaviour of the binary system PEG/Ar at elevated temperatures (343 K and above 373 K) in pressure range from 0 to 33 MPa are presented.

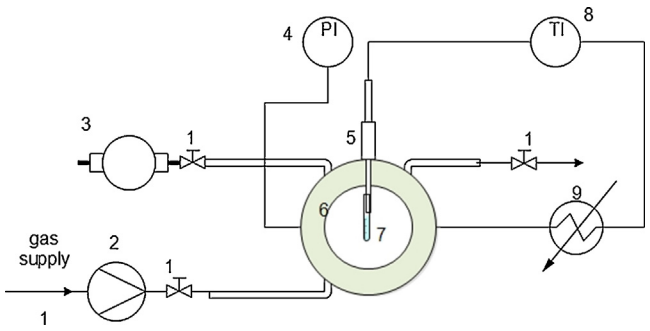

Fig. 1. Apparatus for melting point determination–glass capillary method: 1 valve, 2 gas booster, 3 vacuum pump, 4 pressure indicator, 5 thermocouple, 6 high pressure view cell, 7 glass capillary with sample, 8 temperature indicator, 9 electrical heating.

2. Material and methods

2.1. Materials

Polyethylene glycols (PEGs) were purchased from MERCK (Schuchardt, Hohenbrunn bei München, Germany): PEG 1500 catalogue number (cat. no.) 8.07489, PEG 4000 cat. no. 8.07490, PEG 10 000 cat. no. 8.21881, and PEG 35 000 cat. no. 8.18892. The polymers were in a form of white flakes and were further powdered by a PGSS (Particles from Gas Saturated Solutions) micronisation process using SC CO_2 so that the capillars could be filled with the sample. The micronisation conditions were for PEG 1500: 315 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.

Glass capillars for melting point determination with a length of 75 mm were purchased from Euroglass (Ljubljana, Slovenia).

Argon was obtained from Messer Slovenia, purity 99.996 wt %.

The aforementioned chemicals were used without further purification.

2.2. Equipment

2.2.1. Magnetic suspension balance (MSB)

One of the methods for obtaining solubility and diffusivity data is the gravimetric approach where measurements of gas sorption in the polymer with a high precise balance are performed [12,17].

A magnetic suspension balance (MSB)–RUBOTHERM, with maximum operating temperature of 562 K and operating pressure of 35 MPa and a mass uncertainty $u_{c,m} = 20\ \mu g$, pressure uncertainty $u_{c,p} = 0.5$ MPa and temperature uncertainty $u_{c,t} = 2$ K was used. The detailed description of the equipment and the measuring procedure is reported in the literature [8,19,20].

The balance is separated from the measuring cell, what prevents the damage of the balance and enables measurements under supercritical atmosphere [22].

The solubility and diffusivity of argon in polyethylene glycol at temperatures from 373 to 433 K and in the pressure range from 0 to 33 MPa with increments of approximately 2 MPa with a step-by-step method was investigated using the MSB. Solubility, diffusivity, absorption rate and volume variation for the entire pressure range were determined. The detailed procedure is described in literature [4,8,20].

For stripping measurements the sample was placed inside the MSB and vacuumised. The sample was heated to the experimental temperature and the mass of the substance at vacuum was measured. Then the cell with the sample was pressurised to the maximum pressure (approximately 33 MPa). After equilibrium was reached, the measurement started. The pressure was decreased by 2 MPa in each step (until atmospheric pressure and then vacuumised) and the mass of the sample was observed until reaching the equilibrium. The sample was photographed.

2.2.2. Glass capillary method

The melting points of the unprocessed polyethylene glycol and the polyethylene glycol after processing were determined with a simple Thiele apparatus at atmospheric conditions [23].

The melting points of PEGs under pressure of argon were determined by a glass capillary method in a NWA high pressure view cell (operating up to 90 MPa and 737 K); the apparatus is presented in Fig. 1. The cell is equipped with two saphire windows. The temperature is measured with a thermocouple GHT 1150 Greisinger electronic with an accuracy of ±0.01 K, pressure is measured with a Wika pressure indicator with an accuracy of ±0.001 MPa. The gas is introduced into the cell with a gas booster (type: DLE 75-1-GG-H2) and heated with an electrical heating jacket.

Since PEG was powdered by PGSS process and a small concentration of CO_2 might permanently be captured in the powdered PEG, which could influence the melting point under pressure of argon, the melting points under pressure of argon for unprocessed polymers were determined at pressures approximately 5, 15 and 30 MPa. In order to determine the melting point of the unprocessed polymer, a few polymer flakes, with thickness (0.4 ± 0.02) mm (the thickness was determined with a Mitutoyo calliper 500–123U, CD–15 B with 0.01 mm accuracy) were put in a glass sample container and placed inside the high pressure cell.

2.3. Methods

From the experimental data, the solubility and diffusion coefficients were determined by methods described in literature [4,8,20,24,25].

2.3.1. Solubility

The solubility (S) of argon in PEG was calculated in grams of absorbed argon per gram of PEG.

2.3.2. Diffusion coefficient

The one-dimensional diffusion process has been considered for a limited environment with two parallel plates: $d = 0$ and $d = l$. For a thin plate it is assumed that all of the absorbed gas enters through a single plate in one dimension, which can be described by Fick's second law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial d^2} \tag{1.1}$$

where C (mol/L) is the concentration of the diffusing substance and d is the direction of diffusion. D (cm^2/s) is the diffusion coefficient.