Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

# Density, interfacial tension, and viscosity of polyethylene glycol 6000 and supercritical $CO_2$

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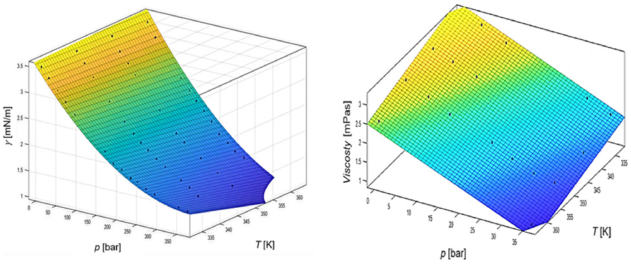
## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Keywords:*
Density
Interfacial tension
Viscosity
Supercritical $CO_2$PEG 6000
$PGSS^{TM}$

## ABSTRACT

In our study, a PEG 6000/$CO_2$ system was used as a model in order to investigate basic thermodynamic and transport data such as density, viscosity and interfacial tension of a $CO_2$ saturated PEG 6000 solution. Additionally, particle size and particle morphology were correlated for the first time with the interfacial tension and viscosity of a PEG 6000 $CO_2$ saturated solution. Binary systems were measured at four temperatures: 333 K, 343 K, 353 K and 363 K from ambient pressure up to pressure of 35 MPa. Density increases linearly with increasing pressure and is significantly reduced with increasing temperature at isobaric conditions. Interfacial tension is reduced when the pressure increases; on the other hand, temperature effect is minimal. Temperature variation has a significant effect on viscosity reduction. The addition of $CO_2$ and consequently increasing pressure result in even lower viscosity.

## 1. Introduction

Supercritical carbon dioxide ($CO_2$) is well established for use as a processing solvent in polymer applications such as polymer modification, the formation of polymer composites, polymer blending, microcellular foaming, polymerization and particle production [1]. In particular, the pharmaceutical and food industries are interested in producing small particles made with improved characteristics The application of pressurized carbon dioxide ($CO_2$) in material processing is a good alternative to reduce the demand of organic solvents. Materials saturated with $CO_2$ under moderate pressure expand in volume, and their physical properties change substantially [2,3].

Particles from Gas Saturated Solution ($PGSS^{TM}$) is a promising high-pressure method that employs supercritical carbon dioxide (scCO2) to produce microparticles [4]. The substance is melted and saturated with dense $CO_2$ in a high-pressure vessel and then expanded via a nozzle into a spray tower. The dense $CO_2$ dissolves to some extent in the melt and reduces interfacial tension and viscosity. After expansion, the solubility of the gas is rapidly reduced by the Joule-Thompson effect when the gas cools. As a result, solid droplets-particles are formed. The $PGSS^{TM}$

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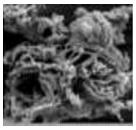
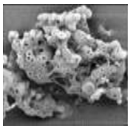
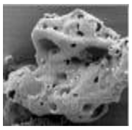
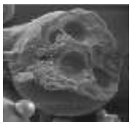
https://doi.org/10.1016/j.supflu.2018.05.012
Received 29 March 2018; Received in revised form 10 May 2018; Accepted 12 May 2018
0896-8446/

**Table 1**
PEG 6000 particle morphology [5].

| Particle shape | Fibres | Micro-foams | Porous irregular particles | Porous spheres | Spheres |
|---|---|---|---|---|---|
| |  |  |  |  |  |
| **Coefficient F** | 0.2 | 0.4 | 0.6 | 0.8 | 1 |

process is suitable for formulation of biologically active drugs and flavors in different biodegradable polymers [5,6]. One of the polymers most often used as a carrier in many applications is polyethylene glycol (PEG), a water-soluble polymer, psychologically acceptable and biocompatible [7]. Kappler et al. [8] developed a regression function (F) that can provide a certain type of PEG 6000 particle morphology as follows:

$$F = 6.9\cdot 10^{-11}\cdot\frac{T\,[K]^{4.247}}{(0.1\cdot p\cdot [MPa]^{0.403})\cdot GTP^{0.105}} \tag{1}$$

where, $T$ is processing temperature in K, $p$ is processing pressure in MPa and $GTP$ is gas to product ratio (CO2 mass flow/polymer mass flow). Relative deviation of results obtained was 14%, at a temperature range of $323\,K < T < 373\,K$ and pressure range of $0.5\,MPa < p < 35\,MPa$. From Table 1, it can be seen that different particle shapes are formed, depending on the processing conditions applied. In our study, a PEG 6000/$CO_2$ system was used as a model in order to investigate the basic thermodynamic and transport data including density, viscosity, and interfacial tension of a $CO_2$ saturated PEG 6000 solution; our results will provide insights for the design of particle formation processes that will help fulfill consumer and economic requirements.

The investigation of thermodynamic properties of binary systems biodegradable polymer/$CO_2$ is a topic currently undergoing intense research. Weidner et al. [9] studied phase equilibrium (solid-liquid-gas) in polyethylene glycol (PEG)-carbon dioxide systems that have been lately frequently employed in the preparation of solid dispersions. Knez et al. [10] measured the solubility and diffusivity of $CO_2$ in PEGs of different molecular weights. Results indicated that solubility of $CO_2$ in PEG increases with increasing pressure and decreasing molar weight. In contrast, diffusion coefficients in the system are mostly influenced by the amount of $CO_2$ already present in the PEG. The same research group has also reported on density and viscosity in binary polyethylene glycol/$CO_2$ systems [11]. They found that increase of dissolved $CO_2$ in the polymer matrix is related to viscosity reduction and density increase. Lee at al. [12] performed rheological measurements using a capillary extrusion rheometer in a Polystyrene (PS)/ $CO_2$ system and observed similar trends of reduction in viscosity when pressure is increased. Kiran et al. [13] simultaneously determinate viscosity, density and phase state of PEG in solutions in n-pentane using a special falling cylinder type viscometer. Gourouillon et al. [14] demonstrate a Vibrating-wire instrument operating on the basis of Archimedes' principle for viscosity, where measuring procedures require previous knowledge of the system density. Interfacial properties of biodegradable polymer melts have been also documented in the literature [15]. Several methods have recently been developed to measure interfacial properties at elevated pressures and temperatures [16–18].

The purpose of the current experiment was to obtain new data on density, interfacial tension and viscosity in systems containing biodegradable PEG 6000 and supercritical $CO_2$ which significantly influence high-pressure separation and formulation processes. To the authors' knowledge, the above-mentioned physical properties of PEG 6000 and supercritical $CO_2$ systems have not yet been measured under these temperature and pressure conditions. Additionally, the data obtained on interfacial tension and viscosity of a $CO_2$ saturated solution with PEG 6000 are here correlated for the first time with particle size and particle morphology [19].

## 2. Experimental

### 2.1. Materials

Polyethylene Glycol (PEG) of molar weight Mw = 6000, cat. no. 8.07491 was provided by MERCK (Germany). The polymer was delivered as solid powder and was used without further purification. Moisture content in PEG 6000 was determined gravimetrically by means of an HB43-S Compact Halogen Moisture Analyzer and was lower than 0.15 wt. %. Disposable capillary *pipettes with* borosilicate glass resistant to thermal shock were provided by Hirschman (Germany). $CO_2$ with purity of 3.0 was obtained from Messer (Slovenia).

### 2.2. Equipment and methods

#### 2.2.1. Density measurements using a density meter with U-tube

The density of $CO_2$ saturated polymer solution was measured by vibrating an Anton Paar DMA 602 U-tube densitometer with an Anton Paar DMA 60 electronic control unit. Nitrogen and Milli Q water were used as calibration fluids. Based on the oscillating time of nitrogen $\tau_{N_2}$ and Milli Q water $\tau_{\mathrm{Milli\,Q\,water}}$, determined experimentally, and known densities $\rho_{N_2}$ and $\rho_{\mathrm{Milli\,Q\,water}}$, the characteristic constant $K$ of the device has been calculated:

$$K = \frac{\rho_{N_2} - \rho_{\mathrm{Milli\,Q\,water}}}{\tau_{N_2}^2 - \tau_{\mathrm{Milli\,Q\,water}}^2} \tag{2}$$

When the U-tube was filled with a sample under the same experimental conditions, the oscillating times $\tau_{\mathrm{polymer/CO_2}}$ were measured and the density of the sample $\rho_{\mathrm{polymer/CO_2}}$ determined by:

$$\rho_{\mathrm{polymer/CO_2}} = K\,(\tau_{\mathrm{polymer/CO_2}}^2 - \tau_{N_2}^2) + \rho_{N_2} \tag{3}$$

In order to reach equilibrium, approximately 5 min was needed at each pressure to stabilize the system [20]. The U-tube was thermostated by means of an external temperature controlled circulating bath, which controls the temperature within $\pm\,5\times 10^{-3}$ K. The temperature and pressure inside the U-tube were measured with an Anton Paar CKT 100 platinum resistance thermometer with an uncertainty of ± 0.01 K and a Nuova Fima EN837-1 manometer with an accuracy of 0.25% for pressures lower than 60 MPa. The reported uncertainty in the density of reference fluids is generally less than 0.1% with an estimation of ± 0.05 kg/m [21]. Detailed operating procedure can be found in the literature [22].

#### 2.2.2. Interfacial tension by a capillary rise method

The interfacial tension of a binary system polymer/$CO_2$ was determined using the capillary rise method in a high-pressure view cell (Sitec AG, Zurich, CH). A capillary of a precisely determined radius (0.4780 mm) was placed vertically inside the cell in a sufficient amount of a polymer sample. The radius of the capillary was determined using a laser coordinate measuring Machine Zeiss 850 UMC. After the desired