



# Interfacial tension and gas solubility of molten polymer polyethylene glycol in contact with supercritical carbon dioxide and argon



Gregor Kravanja, Maša Knez Hrnčič, Mojca Škerget, Željko Knez\*

University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

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## ABSTRACT

Interfacial tension plays a key role in understanding many polymer engineering processes and applications at high pressure. Supercritical fluids are promising media for reducing interfacial tension and increasing the solubility of gas into polymers melts.

An experimental technique modified for studies of the interfacial interactions of liquids in equilibrium with gas in a glass-windowed equilibrium cell based on the means of the capillary rise method was applied for the binary systems of CO<sub>2</sub> + PEG (polyethylene glycol) and argon + PEG. The molecular masses of PEGs differed from  $M_w = 400 \text{ g mol}^{-1}$  up to  $M_w = 10\,000 \text{ g mol}^{-1}$  up to a pressure of 30.0 MPa at a constant temperature of 343 K. This technique was validated by conducting measurements of the interfacial tension between CO<sub>2</sub> and pure water at a temperature of 318 K. The accuracy of the obtained results compared to the ones found in the literature was better than 4%. Additionally, the effect of temperature was also investigated by measuring the solubilities and the interfacial tensions in the systems CO<sub>2</sub> + PEG 1500 and argon + PEG 1500 within the range of temperatures from 328 K up to 363 K.

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## 1. Introduction

Interfacial tension plays a key role in understanding many polymer engineering processes like foaming, blending, coating and particle formation. Generally, low interfacial tension is desired during the polymer foaming processes due to the increase of the nucleation rate and the productions of small and uniform cells [1,2]. Environment-friendly methods like those involving supercritical fluids are promising media for reducing interfacial tension, since it is well known that polymer–gas mixture exposed to high pressure and temperature has a lower interfacial tension than pure polymers. Therefore, by adding gas into polymer, nucleation rate can be controlled by parameters like pressure ( $P$ ) and temperature ( $T$ ). Nucleation rate ( $N$ ) is defined according to the classical nucleation [3,4] theory:

$$N = Sf \exp \left[ \frac{16\pi\gamma^3}{3kT\Delta P^2} \right] \quad (1.1)$$

where  $f$  is the frequency of the gas molecules joining the nucleus,  $S$  is gas concentration,  $\gamma$  is the interfacial tension between the

polymer phase and nucleation bubble phases,  $T$  is the temperature and  $\Delta P$  is the pressure difference across the polymer–gas interface. Another field requiring knowledge of predicting interfacial properties between polymers and supercritical fluids involves particle formation [5–9]. Interfacial tension is a crucial parameter when designing several processes connected with particle size and the encapsulations of drugs.

To date, a substantial body of literature exists on the interfacial tension of polymer melts, but little data can be found about investigations of the interfacial tensions of molten polymers at high pressure in contact with supercritical carbon dioxide. There is, to our knowledge, no data on the interfacial tension of binary systems containing molten polymer and noble gas at high pressure. The reasonable choice for using argon under supercritical conditions as an alternative instead of carbon dioxide during polymer processing is due to its inactivity, easy accessibility, very low thermal conductivity, and also the easily accessible critical point ( $T_c = -122.46^\circ\text{C}$ ,  $P_c = 4.863 \text{ MPa}$ ) [10]. The review by Janssen et al. [11] provides extensive information on useful processing aspects and applications of polymers melts at high pressures, where the high diffusivity of CO<sub>2</sub> and the low interfacial tension are key factors in determining a wide range of applications. Mahmood et al. [12] investigated the interface of molten polylactide (PLA) by analyzing sessile drops within high-pressure and high temperature visualization chamber from 6.89 to 20.68 MPa and from 463

\* Corresponding author. Tel.: +386 2 22 94 461; fax: +386 2 2516750.  
E-mail address: [zeljko.knez@um.si](mailto:zeljko.knez@um.si) (Ž. Knez).

to 473 K, respectively. Harrison and co-authors [13] studied the effects of various surfactants on the interfacial tension between 600 MW polyethylene glycol (PEG) and supercritical CO<sub>2</sub> at 318 K on the basis of measurements by a novel tandem variable-volume pendant drop. Interesting work was carried out by Carbone et al. [14,15] where interfacial tension, solubility, diffusivity and specific volume of molten polycaprolactone/CO<sub>2</sub> solutions were simultaneously measured to reduce errors by using a custom-designed measurement device consisting of a rod to which polymer–gas solution was stuck (by the pendant drop method) and placed within a magnetic suspension cell. Gutiérrez et al. [2] studied interfacial tension and glass transition of polystyrene in supercritical CO<sub>2</sub> within the pressure range from 0 to 9 MPa, and temperatures from 303.15 to 313.15 K by the pendant drop method. O'Neill et al. [16] found the solubilities of polymers in CO<sub>2</sub> to be related to their surface tensions under atmospheric conditions, which were later investigated under high pressure. Although it is difficult to achieve accurate and comparable data when modeling the thermodynamic properties of molten polymers at high pressures with experimental ones Enders et al. [17,18] presented the Cahn–Hilliard theory with equations that stated (the original statistical associating fluid theory, the perturbed-chain statistical associating fluid theory or the Sanchez–Lacombe lattice theory) in order to describe both, the solubility of carbon dioxide in polystyrene, and the interfacial properties between the liquid mixture and the pure gas phase.

Currently only a few methods have been reported and realized for the measurements of interfacial tension on the surface between polymer melt and supercritical fluid [12,19]. The more commonly used are drop shape methods like pendant, sessile and spinning drop which are based on analyzing the shape of a drop by fitting experimental images to the theoretical Laplacian curve for known interfacial tension values using nonlinear optimization [20–22]. Those requiring less samples, are applicable to both air–liquid and liquid interfaces, and are versatile and applicable to various situations [20–22]. Despite the general advantages and the good accuracies of the results obtained by such techniques, the performances and sensitivities decrease drastically when the drop shape becomes close to spherical [23,24]. Another problem is presented by the evaporation of small drops at high temperatures which might decrease accurate values for interfacial tension and specific volume [25–28]. Therefore, in our previous research [29] an optimized experimental setup was developed by the sophisticated capillary rise method for investigating viscous polymers melts under high temperature and pressure. It was shown to be a good alternative method due to its simplicity, accuracy and low cost operation. The choice of investigating the interfacial tension of polymer PEG is connected to its importance in the food and pharmaceutical industries due to its unique characteristic properties like: high solubility in organic and aqueous solvents, no toxicity, immunogenicity and antigenicity, and the high flexibility and hydration of the polymer chain [30]. In addition, polyethylene glycol is used in mixtures with other polymers, such as polystyrene, and CO<sub>2</sub> in the foaming formation of polymer blends [31]. Foaming of these blends can result in remarkable foam morphologies with bimodal cell size distributions and new material properties [32].

During our research, special attention was focused on simultaneous acquisition of fundamental thermodynamic properties like interfacial tension, solubility and density of molten polymer polyethylene glycol in contact with supercritical CO<sub>2</sub> or argon. Interfacial tension between the PEGs of several molecular masses differing from  $M_w = 400 \text{ g mol}^{-1}$  up to  $M_w = 10\,000 \text{ g mol}^{-1}$  were measured during the presented work for the pressure range from 0.1 MPa up to 30.0 MPa at a constant temperature of 343 K.

## 2. Experimental

### 2.1. Materials

Polyethylene glycols (PEGs) of molecular masses,  $M_w = 400 \text{ g mol}^{-1}$  catalogue number (cat. no. 8.07485),  $M_w = 1000 \text{ g mol}^{-1}$  cat. no. 8.17009,  $M_w = 1500 \text{ g mol}^{-1}$  cat. no. 8.07489,  $M_w = 4000 \text{ g mol}^{-1}$  cat. no. 8.07490,  $M_w = 6000 \text{ g mol}^{-1}$  cat. no. 8.07491,  $M_w = 10\,000 \text{ g mol}^{-1}$  cat. no. 8.21881 were provided by MERCK (Germany). The polymers were delivered as liquids and were used without further purification. The greater moisture content in the polymers was determined gravimetrically by the means of a HB43-S Compact Halogen Moisture Analyzer and was lower than 0.15 wt.% for each polymer. Disposable capillary pipettes with borosilicate glass resistant to thermal shock were provided by Hirschmann (Germany). CO<sub>2</sub> (99.9% purity) and argon (99.9% purity) were obtained from Messer (Slovenia).

### 2.2. Equipment and methods

In our previous research [29] an optimized experimental setup was developed by the sophisticated capillary rise method which reflects a compromise between the competing claims of accuracy, low cost operation, and simplicity. In this study we have upgraded our previous experimental setup by determining the equilibrium heights by the capillary rise (CR) method within a high pressure view equilibrium cell (Fig. 1) and the required densities of the investigated systems by a method involving magnetic suspension balance (MSB) (Fig. 2).

#### 2.2.1. High pressure apparatus for the vapor–liquid equilibrium measurements

By means of the capillary rise method accurate data of the equilibrium heights of molten Polyethylene glycols were measured within a high pressure view equilibrium cell made of stainless steel (Sitec AG, Zurich, CH), previously described in literature [33]. The cell volume is 500 mL and is designed for a pressure of 50 MPa and temperature of 423 K. The pressure inside the cell was measured by an electronic pressure gauge (WIKA Alexander Wiegand GmbH & Co. KG, Alexander-Wiegand-Straße, Klingenberg, Germany). The temperature of the cell was kept constant using a heating jacket and was observed using calibrated thermocouple immersed in the cell. The uncertainty of the pressure was 0.01 MPa and the total uncertainty of the temperature was 0.1 K.

#### 2.2.2. Gravimetric method with magnetic suspension balance (MSB)

The Capillary Rise method, as well as many other methods designed for obtaining the desired values for interfacial tension, requires accurate knowledge about the densities of the investigated systems. Densities and solubilities of the carbon dioxide and argon saturated solutions of molten polyethylene glycols were measured by a gravimetric method involving magnetic suspension balance (MSB, RUBOTHERM, Germany). The applied MSB is designed for a maximum operating pressure of 35 MPa and operating temperature of 562 K with a mass uncertainty of  $u_{c,m} = 20 \text{ } \mu\text{g}$ , pressure uncertainty of  $u_{c,p} = 0.5 \text{ MPa}$  and temperature uncertainty of  $u_{c,t} = 2 \text{ K}$  [36]. Such an accuracy is possible due to the location of the balance outside the measuring cell, under normal conditions of pressure and temperature. The measuring force is transmitted contactless from the measuring chamber to microbalance by magnetic suspension coupling [34]. The measuring cell of MSB is also provided with a window, which allows knowledge of the sample and estimation of volume modifications during the sorption measurements. A detailed description of the device and of the working procedure can be found in literature [35,36].

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