# On the unexpected non-monotonic profile of specific volume observed in PCL/CO$_2$ solutions

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## ABSTRACT

Recently, the specific volume of molten solutions of polycaprolactone and carbon dioxide (PCL/CO$_2$) was measured by coupling gravimetric measurements with the observation of the swelling of a pendant drop. Quite interestingly, this approach highlighted a non-monotonic dependence of the specific volume of the solution on CO$_2$ pressure. Herein, in order to get a molecular insight into this experimental finding, Raman spectroscopy has been adopted for the investigation into PCL/CO$_2$ solutions at several pressures. This investigation has shown that – due to the interactions of CO$_2$ and PCL - polymer-associated and non-associated CO$_2$ species can be found in the solution. Furthermore, the dependence of CO$_2$ association on gas pressure has been analysed and invoked for the discussion of the non-monotonic evolution of the specific volume with increasing CO$_2$ pressure.

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## 1. Introduction

Specific volume of polymer/gas solution is a relevant fundamental property in the study and the optimization of several polymer processing technologies, such as gas foaming, blending and extraction reaction. Dilatometry is the most common technique to measure the specific volume of neat polymers as a function of temperature and pressure [1]. Nevertheless, the experimental evaluation of specific volume of polymer/gas solutions is not always straightforward. In fact, despite several techniques for measuring polymer swelling in the presence of high pressure gas and at temperatures below glass transition temperature have been described in literature (e.g., the in situ optical observation, where the length change in one or more dimensions is measured in the presence of high pressure gas [2,3]), just few data have been reported so far regarding the measurement of specific volume of polymeric solutions at temperatures higher than the glass transition temperature [4,5]. Recently, some of the authors have proposed a purely experimental approach for the simultaneous measurement of solubility, diffusivity, specific volume and surface tension of molten polymer/gas solutions, which is based on the coupling of gravimetric measurement and the observation of a pendant drop [6], without resorting to any predictive modelling, thus ensuring the reliability of the aforementioned measured properties. Tests performed by using the coupled technique revealed that the specific volume of molten poly($\varepsilon$-caprolactone)/CO$_2$ solutions shows a non-monotonic profile in the investigated experimental pressure and temperature range (see Fig. 1) [7].

Actually, other molten/rubbery polymer-CO$_2$ systems have been investigated in the literature in terms of dependence of specific volume of the mixture on the pressure of carbon dioxide, although still few data of this type are available. At the best of authors' knowledge, there has not been reported any system displaying the non-monotonic behaviour observed in the case at hand. As an example, a monotonically increasing dependence is reported in literature for CO$_2$-PEG system and a monotonically decreasing dependence is reported for CO$_2$-PP system [5].

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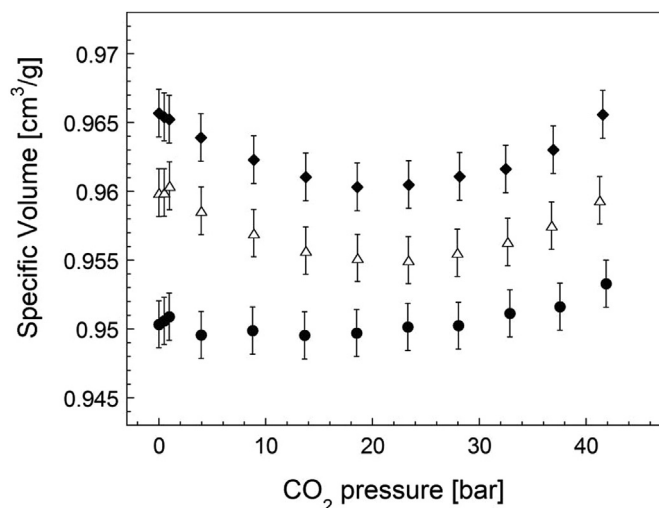
**Fig. 1.** Specific volume of the solution PCL/CO$_2$ as a function of CO$_2$ pressure, at 80 °C ( ● ), 90 °C ( △ ) and 100 °C ( ◆ ). Data from Ref. [7].

According to Kazarian et al., effects of CO$_2$ on polymers (e.g. swelling, plasticization) are not a purely physical phenomenon but are often the result of specific interactions between the gas molecules and the polymer [8]. For this reason, spectroscopic techniques, such as Attenuated Total Reflectance (ATR), Fourier Transformed Infrared (FTIR) and Raman spectroscopy, are being widely used for the investigation of sorption behaviour of CO$_2$ (and of other low molecular weight penetrants) in polymers, as they provide useful information on both local gas concentration and on possible specific polymer/gas interactions. Actually, investigations based on the use of ATR and FTIR have revealed that CO$_2$ interacts with most polymers [9,10] as specific spectroscopic features of the solution (such as the observation of the splitting of the peak assigned to CO$_2$ bending mode) have been demonstrated to be the evidence of the interaction between the gas molecules and the polymer [8,9].

In this work we present the results of the investigation of molten PCL/CO$_2$ solutions based on Raman spectroscopy. Raman spectra were collected from a pendant drop of molten PCL exposed to CO$_2$ at several pressures. The interaction between CO$_2$ and the polymer has been proved; furthermore, the dependence of PCL/CO$_2$ association on gas pressure has been analysed, thus providing an interesting interpretation for the experimental observation of the minimum in specific volume profiles.

## 2. Experimental methods

### 2.1. Materials

Poly($\varepsilon$-caprolactone), a biodegradable polymer with a melting point of ca. 60 °C, was supplied by Perstorp AB (PCL CAPA 6800) and used as received. A hemispherical polymer drop was created on the base of a titanium rod with a diameter of 3.15 mm according to the procedure described elsewhere [6]. CO$_2$ with a purity of 99.5% was purchased by Linde, Germany.

### 2.2. Testing procedure

The PCL pendant drop was set in a high temperature/high pressure (HT/HP) chamber equipped with three sight windows. Then, the HT/HP chamber was heated up to 90 °C and evacuated in order to remove moisture from the polymer before starting the

test; in these conditions, by adopting the optical setup described in Refs. [11], a Raman spectrum was acquired from molten pure PCL. CO$_2$ pressurization was then started and, immediately after opening the valve connecting the syringe pump with the chamber, Raman spectra were recorded each 30 s, until the spectra did not show any variation in time, defining the attainment of equilibrium. Pressure was increased in a stepwise manner up to 60 bar. All spectra were acquired by focussing onto the middle of the drop, in the Raman shift range of 480 cm$^{-1}$ up to 2270 cm$^{-1}$, with the same camera settings and with an exposure time of 6 s. Furthermore, a Raman spectrum of gaseous CO$_2$ has been collected by filling the chamber (without the drop) with pressurized gas by using the same settings. Raman spectra of CO$_2$-saturated PCL at several pressures have been analysed and compared to those of molten PCL and pure gaseous CO$_2$.

## 3. Results and discussion

### 3.1. Analysis of PCL/CO$_2$ spectra

The spectra of neat PCL, of pure gaseous CO$_2$ and of CO$_2$-saturated PCL (for the sake of clarity, only one spectrum of the solution, e.g. at 40 bar, has been reported) are shown in Fig. 2. The Raman spectrum of pure PCL exhibits three well-defined peaks at 1295 cm$^{-1}$ (CH$_2$ wagging mode, $\omega_{CH_2}$), at 1430 cm$^{-1}$ (CH$_2$ scissoring mode, $\delta_{CH_2}$) and at 1722 cm$^{-1}$ (C=O stretching mode, $\nu_{C=O}$), a small peak at 1151 cm$^{-1}$ assigned to stretching vibration of ethereal C–O–C, a series of peaks between 1033 and 1107 cm$^{-1}$, which have been assigned to the skeletal stretching, and a typical fingerprint in the region between 500 and 1000 cm$^{-1}$ [12]. The spectrum of gaseous CO$_2$ is characterized by two major peaks located at 1388 cm$^{-1}$ (upper Fermi dyad, $\nu_u$) and 1285 cm$^{-1}$ (lower Fermi dyad, $\nu_l$) [13]. The spectrum of the CO$_2$-saturated PCL shows, beside the typical pattern of PCL, the presence of the CO$_2$ upper and lower Fermi dyads, which appear slightly shifted as compared to the positions in the spectrum of the gas phase [13]. More interestingly, the spectrum of the PCL/CO$_2$ solution shows two peaks located at 648 and 676 cm$^{-1}$, which are neither present in the spectrum of neat polymer nor in the spectrum of pure gas. As discussed by Cabaço et al. [14], these two peaks can be assigned to the in-plane and the out-of-plane CO$_2$ bending modes which become Raman-
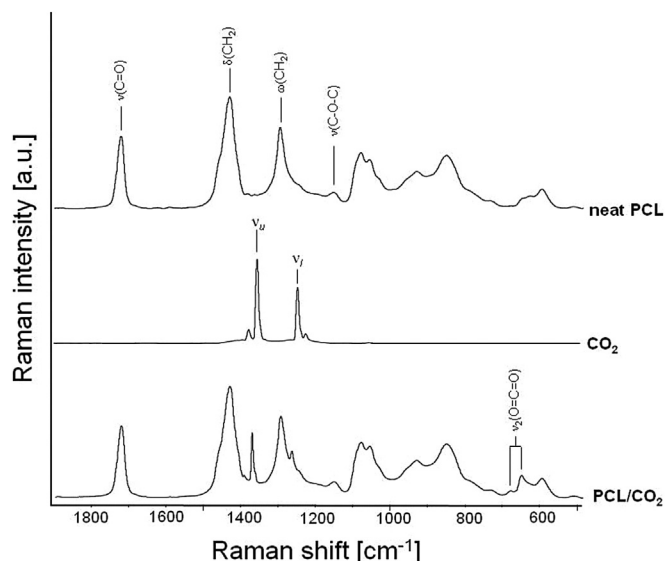


**Fig. 2.** Raman spectra of CO$_2$, neat PCL and PCL/CO$_2$ solution at 40 bar and 90 °C.

active as a result of the interaction between $CO_2$ molecules and the polymer. In fact, the molecular interaction between the $CO_2$ molecule and the polymer matrix causes the $D_{\infty h}$ symmetry loss of the $CO_2$ molecule, the double degeneracy of the $\nu_2$ mode (i.e. in-plane and out-of-plane) being removed [8,9]. In IR spectra, this results in the observation of the splitting of the band corresponding to the $CO_2$ $\nu_2$ mode, as observed for the first time by Kazarian et al. [8]. In the case of the solutions investigated by Raman spectroscopy, the $D_{\infty h}$ symmetry loss of the $CO_2$ molecule induced by the interaction results, more strongly, in the activation of the bending vibrations in the Raman spectrum (i.e., $\nu_2$ bending mode of gaseous $CO_2$ being Raman-inactive). The analysis of the interaction site on polymer backbone supported by *ab-initio* modelling will be discussed in a forthcoming paper.

As the peaks observed at 648 and 676 $cm^{-1}$ can be assigned to $CO_2$ bending modes, which become Raman active by the interaction process, their presence in the Raman spectra of $CO_2$-saturated PCL suggests that carbon dioxide is present in PCL in at least two 'populations', as also reported by Nawalade et al. [10]: one 'polymer-associated', i.e. interacting with the PCL, and the other 'non-associated'.

In particular, the interaction-induced bending peaks (both in-plane and out-of-plane $\nu_2$) are correlated to the associated $CO_2$ species while the Fermi dyads represent the overall dissolved $CO_2$ population, made up of both associated and non-associated species. Hence, the ratio of the intensity of the interaction-induced peaks to the intensity of the Fermi dyad can be adopted to quantify, at each pressure, the contribution of the associated species to the overall $CO_2$ population. The dependence of the ratio of the intensity of the peaks at 648 and 676 $cm^{-1}$ ($I_{\nu2}$) to the intensity of the upper Fermi dyad ($I_{vu}$) with $CO_2$ pressure are depicted in Fig. 3. The ratio has been found to decay significantly with $CO_2$ pressure, thus indicating that the relative contribution of associated $CO_2$ to the total $CO_2$ amount within the mixture gradually decreases with increasing pressure. In the whole investigated pressure range $I_{vu}$ was found to increase linearly with pressure [11].

In the light of these spectroscopic results, it is interesting to discuss the presence of the minimum in the profile of the specific volume of the PCL/$CO_2$ solution as a function of pressure. In fact, the specific volume of the mixture $\widehat{V}_{MIX}\big|_{T, P_{TEST}, \omega_{PCL}}$, at the test

temperature and pressure and at the $CO_2$ mass fraction dictated by sorption equilibrium, can be expressed as follows:

$$\widehat{V}_{MIX}\big|_{T, P_{TEST}, \omega_{CO_2}} = \widehat{V}_{MIX}\big|_{T, P_{REF}, \omega_{CO_2}}$$
$$+ \int_{T, P_{REF}}^{T, P_{TEST}} -\beta\big|_{T, P, \omega_{CO_2}} \cdot \widehat{V}_{MIX}\big|_{T, P, \omega_{CO_2}} dP$$

with

$$\widehat{V}_{MIX}\big|_{T, P_{REF}, \omega_{CO_2}} = \left(\omega_{PCL}\widehat{V}'_{PCL} + \omega_{CO_2}\widehat{V}'_{CO_2}\right)_{T, P_{REF}}$$

$$\widehat{V}_{MIX}\big|_{T, P, \omega_{CO_2}} = \left(\omega_{PCL}\widehat{V}'_{PCL} + \omega_{CO_2}\widehat{V}'_{CO_2}\right)_{T, P}$$

In the previous expressions $P_{REF}$ is 1 atm, $\omega_i$ and $\widehat{V}'_i$ represent, respectively, the mass fraction and the partial specific volume of component '$i$' and $\beta$ is the isothermal compressibility of the mixture volume. Thus, the observed reduction of the specific volume of the mixture, in the range of lower pressure values, could be related to the fact that the partial specific volume of $CO_2$ in the mixture is lower than the partial specific volume of the polymer (negative association volume) and/or could be a consequence of the isothermal compressibility of the mixture. Actually, the polymer-associated and the non-associated $CO_2$ species likely display different partial specific volumes. In particular, a lower partial specific volume − possibly even lower than partial specific volume of PCL - is expected in the case of polymer-associated $CO_2$ species, due to the interaction that keeps the $CO_2$ molecules closer to interacting sites on polymer backbone thus contributing a lower volume upon mixing as compared to non-associated species. On this basis, the initial decrease of specific volume of the mixture as a function of pressure can be ascribed, at least in part, to the low partial specific volume contributed by the fraction of associated population. Conversely, as the pressure increases, the ratio of associated species to the non-associated ones gradually decreases - the overall $CO_2$ signal still increasing − and the observed upturn in the value of specific volume can be tentatively attributed to the
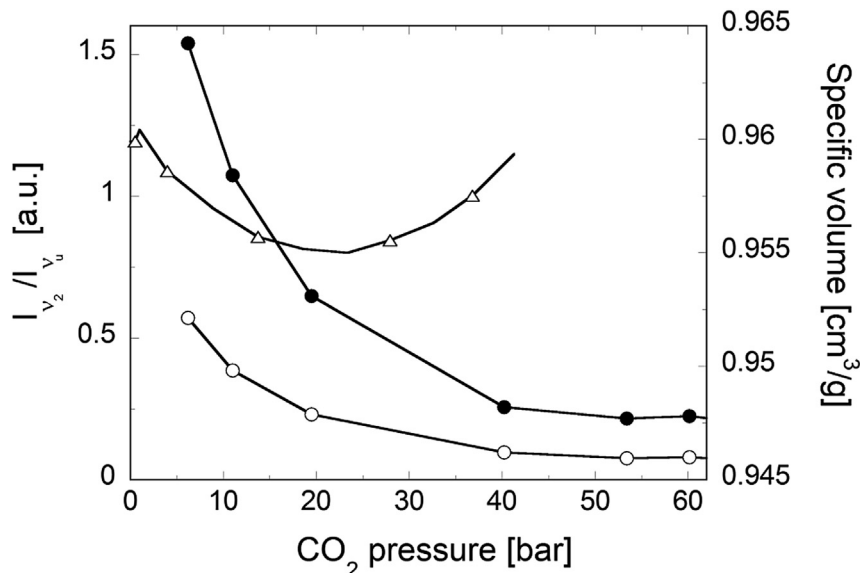


**Fig. 3.** Contribution of associate species to overall $CO_2$ population: intensity of the interaction-induced peaks at 648 (full circles) and 676 $cm^{-1}$ (open circles) normalized to the intensity of the upper Fermi dyad as a function of $CO_2$ mass fraction. Specific volume (triangles) data from Ref. [7]. Lines are a guide to the eye.

increase of the partial specific volume of $CO_2$ related to the increased fraction of non-associated $CO_2$ molecules.

## 4. Conclusions

Raman spectra collected from a pendant drop of molten PCL exposed to high pressure $CO_2$ have been adopted to probe the interaction between the gas and the polymer. The spectra of the PCL/$CO_2$ solutions at different pressures have shown two peaks located at 648 and 676 $cm^{-1}$, which have been assigned to the in-plane and the out-of-plane $CO_2$ bending modes becoming Raman-active by the interaction with the polymer. Interaction-induced peaks have been adopted to analyse the effects of pressure on association: in particular, the contribution of associated species to overall $CO_2$ population has been evaluated and found to decrease with $CO_2$ pressure. On this basis, one can provide a possible explanation for the observation of a minimum in specific volume of PCL/$CO_2$ solutions with pressure by considering that the partial specific volume of the associated $CO_2$ species is possibly both lower than that of polymer and of that of not associated $CO_2$ species. This conclusion has to be further supported by deepening the vibrational spectroscopy analysis and, eventually, by investigating the change of volume at a molecular level accompanying the interaction of carbon dioxide with specific sites on the polymer backbone. Further spectroscopic analysis (e.g. determination of interaction site on polymer backbone), along with deeper insight on the interaction mechanism, will be discussed in a forthcoming paper.

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