

Mass transport and physical properties of polymeric methylene diphenyl diisocyanate/CO₂ solutions



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ARTICLE INFO

Article history:

Received 3 August 2017

Received in revised form

19 October 2017

Accepted 20 October 2017

Available online 21 October 2017

Keywords:

Isocyanate

PMDI

CO₂

Solubility

Diffusivity

Interfacial tension

Specific volume

Polyurethane foam

ABSTRACT

Polyurethane foams are typically obtained by reacting a polyisocyanate with a polyol and the foamed structure derives from a blowing reaction concurrent to the polymerization reaction. The blowing stage makes use of chemical and physical blowing agents, among which ozone-depleting or flammable gases are being substituted with eco-friendly and safe ones, such as CO₂. To allow a more educated use of CO₂ as a physical blowing agent in polyurethane foams, we herein investigate the CO₂ sorption in polymeric methylene diphenyl diisocyanate (PMDI), by using a fully experimental, coupled gravimetry-Axisymmetric Drop Shape Analysis. Solubility, mutual diffusivity, specific volume and interfacial tension of PMDI/CO₂ solutions in contact with CO₂ have been measured at 35 deg C and at CO₂ pressures up to 6500 kPa. Effects of CO₂ on PMDI were also evaluated by using Gel Permeation Chromatography and Fourier Transform Infrared spectroscopy.

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1. Introduction

Polymeric methylene diphenyl diisocyanate (PMDI), together with polyols, is a key component in the synthesis of flexible, semi-rigid and rigid polyurethane foams (PUFs). Typical applications of flexible PUFs are cushioning in furniture and in automotive [1]. Rigid PUFs are thermal insulating materials, used in construction and in appliances like refrigerators [2].

PUFs are obtained by two simultaneous reactions: the polymerization reaction (addressed to, typically, as “gelling reaction”) between the polyol and the PMDI to give urethanes, and the “blowing reaction” between PMDI and water to give unstable carbamic acid that decomposes to amine and CO₂ as a by-product, eventually inflating the polymer [2]. Catalysts, chain extenders, surfactants and physical blowing agents (PBAs), are usually added to the polyol to fine tune the reactions kinetics and optimize the

final pore structure and foam density. Regarding the PBAs, CFCs and HCFCs, now banned because of their environmental impact, have been replaced by flammable hydrocarbons (e.g. pentane), with the related safety issues. A good alternative to flammable PBAs, is CO₂, due to its zero Ozone Depletion Potential (ODP) and its large availability and safety.

As already discussed in Di Caprio et al. [3] for polyol/CO₂ solutions, knowledge of the physical properties, such as solubility, mutual diffusivity, interfacial tension and specific volume of PMDI/CO₂ solutions is fundamental to properly design the foaming process and to optimize the foam structure. As a matter of fact, the optimization of the foaming process involves the control of the fluidodynamic behavior of the polymer containing the dissolved gas at high concentration and at thermodynamic conditions able to promote the nucleation and growth of gas bubbles in the reacting liquid. The nucleation and growth rates, which determine the final morphology of the foam, are related to the physical and transport properties of the polymer/gas system. In particular nucleation rate depends on gas concentration and the surface properties of the fluid/gas interface [4–8], while the growth rate on [9–13] gas

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diffusivity, and the surface and viscoelastic properties of the matter around the bubble.

To the best of our knowledge, no papers addressed these properties of PMDI/CO₂ solution to date. In this paper, we report the measurement of CO₂ solubility in PMDI as well as mutual diffusivity, specific volume and interfacial tension of PMDI/CO₂ solution by using a recently developed equipment based on the coupled sorption-ADSA [3,14,15]. Measurements have been performed at 35 deg C and at CO₂ pressures up to 6500 kPa.

2. Experimental section

2.1. Methods

The coupled sorption-ADSA experiments were performed by using a magnetic suspension balance (MSB) (Rubotherm Präzisionsmesstechnik GmbH, Germany), equipped with a high pressure and temperature (HT-HP, up to 250 deg C and 13500 kPa) view cell. The simultaneous measurement was conducted on a crucible containing 0.3 g ca. of PMDI/CO₂ solution (for weight monitoring) and on a custom-designed Teflon rod to which the PMDI/CO₂ solution drop is stuck (for ADSA). In particular, the crucible hangs from the hook of the MSB, while the rod is fixed inside the cell in such a way as to avoid any interference with the gravimetric measurement and to allow the reliable continuous acquisition of the drop shape (see Fig. 1a.). Drop changes in volume and shape were observed through two optical quality windows, by using an adjustable high resolution CCD camera (BV-7105H, Appro), equipped with a modular zoom lens system (Zoom6000, Navitar). The CCD camera is connected to a computer, and a commercial software (FTA32 Video 2.0, First Ten Angstroms) is used to analyze drop profile [3,14,15]. Furthermore, in order to achieve the optimal threshold background for digitizing the drop image, a uniform bright background was provided by light emitting diodes. Full details of the equipment and the description of the preliminary experimental phases, such as drop preparation, optimization of CCD parameters and image calibration (pixel.μm⁻¹ calibration and aberration correction), are given in Ref. [14].

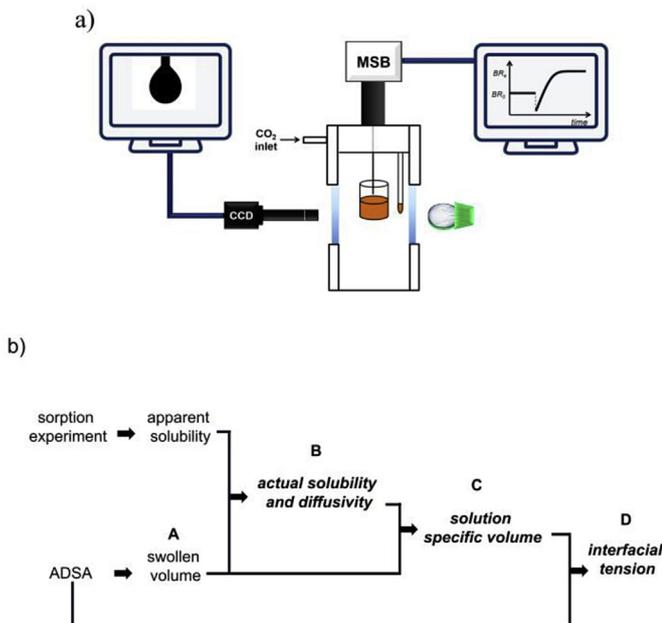


Fig. 1. (a) Schematic illustration of the experiment and (b) data flow used in the coupled sorption-ADSA measurement.

The data flow adopted for the elaboration of the data acquired during the coupled sorption-ADSA measurement is illustrated in Fig. 1b.

Sorption and ADSA experiments were carried out by isothermal pressure increments up to 6500 kPa and at 35 ± 0.1 deg C, which is the typical temperature utilized in the industry to conduct polyurethane foam synthesis in presence of CO₂ at high pressure, after having placed both the crucible containing the PMDI and the rod with the PMDI drop in the HT-HP view cell and having evacuated the system for 2 h at 10^{-3} Pa. In detail, sorption measurements were performed by step-wise increments of the gas pressure (500 kPa steps ca.), after the attainment of equilibrium sorption in the previous step. Concurrently, during each pressure step, image acquisition of the pendant drop was performed every 10 min.

2.2. Materials

PMDI technical grade (Table 1), contains 45% of pure MDI and 55% of higher molecular weight MDI oligomers, was supplied by DOW Italia S.r.l (Correggio, RE, Italy) within the LIFE13-EN/IT/001238 project (<http://ec.europa.eu/environment/life/>, www.dow.com/k12) and used “as received”. High-purity grade CO₂ (99.95% pure) was supplied by SOL (Naples, Italy).

The isocyanate equivalent weight is defined as the molecular weight of the isocyanate functional group per the NCO content expressed as the weight fraction of the NCOs in the isocyanate, as follows [1].

$$\text{equivalent weight} = \frac{MW_{NCO}}{\text{weight fraction}_{NCO}} = \frac{42.0}{0.311} \text{ g/eq} \quad (1)$$

2.3. Data treatment

Data treatment is described in the following, according to the measurement flow chart reported in Fig. 1B and as detailed in Pastore Carbone et al. [14].

2.3.1. Evaluation of the swelling of the polymer/gas solution

To correct sorption data for buoyancy effects, the actual volume of the sample contained in the crucible, $V_c(p)$, is needed. At equilibrium (A in Fig. 1b), it can be calculated from drop volume, as by Eq. (2):

$$V_c(p) = \frac{V_d(p) - V_d^0}{V_d^0} V_c^0 + V_c^0, \quad (2)$$

where, $V_d(p)$, is the volume of the CO₂-saturated PMDI drop calculated by integrating the drop profile, while V_d^0 and V_c^0 are, respectively, the volume of the drop and the volume of the PMDI contained in the crucible at initial conditions (under vacuum). It was assumed that, at equilibrium, drop curvature has negligible effects on specific volume and local gas concentration [16] and, consequently, that the drop and the sample in the crucible reach the same volume per unit mass of initial PMDI.

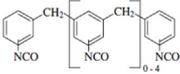
2.3.2. Actual solubility and diffusivity

The actual CO₂ weight fraction in the PMDI/CO₂ solution (w_{ACT}), is calculated by Eq. (3):

$$w_{ACT}(p) = \frac{W_{ACT}^{gas}(p)}{W_c^0 + W_{ACT}^{gas}(p)}, \quad (3)$$

where W_c^0 is the initial weight of the sample contained in the

Table 1
Properties of the “as received” PMDI.^a

CAS number	9016-87-9	equivalent weight/g.eq ⁻¹	135
chemical formula	C ₁₅ H ₁₀ N ₂ O ₂ to C ₄₇ H ₃₀ N ₆ O ₆	NCO content	31.1%
structural formula		functionality	2.7
physical state (appearance)	liquid	viscosity/mPa.s (25 deg C) ^b	190
color	dark brown	acidity ^c	0.02 %HCl

^a IUPAC name of PMDI: Polymeric 1,1'-Methylenebis(4-isocyanatobenzene).

^b (Manufacturer technical data sheet: http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0034/0901b80380034d8b.pdf?filepath=polyurethane/pdfs/noreg/109-50101.pdf&fromPage=GetDoc - accessed October 2017).

^c Defined as reported in Ref. [1].

crucible (as measured by an analytical balance) and W_{ACT}^{gas} is the actual weight gain, as calculated by Eq. (4):

$$W_{ACT}^{gas}(p) = BR_e - BR_e^0 + \rho_{gas}(p)[V_c(p) + V_h]. \quad (4)$$

Here, BR_e is the MSB reading at equilibrium at each pressure (attainment of homogeneous CO₂ concentration), BR_e^0 is the initial MSB reading at equilibrium (under vacuum), ρ_{gas} is the CO₂ density in the gas phase [17], V_h is the volume of crucible and of hook that was previously determined by evaluating the buoyancy effect in a blank test with helium.

The average mutual diffusivity (\bar{D}) in each step-wise sorption experiment was calculated by fitting sorption kinetics data with the Fickian equation (Eq. (5)) [18]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\bar{D}(2n+1)^2 \pi^2 t / L^2\right\}, \quad (5)$$

where M_t is the mass of the CO₂ sorbed at time t , M_∞ is the mass of the CO₂ sorbed at equilibrium and L is the actual sample thickness (sample is exposed to the gas phase on one side only) calculated as the average between the initial and final thicknesses of the sample as evaluated from the corresponding value of $V_c(p)$. M_t has been calculated as $BR_{(t)} - BR_{(0)}$ and M_∞ has been calculated as $BR_{(\infty)} - BR_{(0)}$, where $BR_{(0)}$ is the balance reading just after the pressurization, $BR_{(t)}$ is the balance reading at time t , $BR_{(\infty)}$ is the balance reading at equilibrium. The value of \bar{D} calculated using Eq. (5) has been taken as representing a reasonable estimate of the value of the CO₂ mutual diffusivity, $D(C)$, at a carbon dioxide concentration, C , that is the arithmetic average of the concentration at the start and at the end of sorption experiment. The fitting procedure has been carried out by using an optimization procedure based upon the descent gradient method, which minimizes the relative residual as a function of the model parameters, and it has been implemented in a Matlab code.

2.3.3. Evaluation of specific volume of the PMDI/CO₂ solution

The specific volume of the PMDI/CO₂ solution, v_s , was calculated as by Eq. (6):

$$v_s(p) = \frac{V_c(p)}{W_c(p)} = \frac{V_c(p)}{\left(\frac{W_c^0}{1 - w_{ACT}(p)}\right)}, \quad (6)$$

with $W_c(p)$ being the actual weight of the sample contained in the crucible.

2.3.4. Evaluation of interfacial tension of the polymer/gas solution in contact with CO₂

In order to determine the interfacial tension of the separating

surface between the PMDI/CO₂ solution and the surrounding CO₂, γ , the specific volume of the solution at different pressures, $v_s(p)$, as determined according to Eq. (6). (C in Fig. 1b), was used as input to the drop analysis software. Based on the Bashforth–Adams equation, the software performs the calculation of the equilibrium value of interfacial tension at each pressure by fitting the shape of the experimental drop to the theoretical drop profile according to the Laplace equation, properly modified to account for the action of the gravitational field [19–21]. It is worth of note, here, that typically, in the literature, interfacial tension data at high gas pressure are gathered without information of the actual drop weight, leading to errors in the calculation.

2.4. Gel Permeation Chromatography analysis

Gel Permeation Chromatography (GPC) analysis was conducted, on the “as received” PMDI and on the PMDI recovered from the crucible after the sorption campaign (addressed to, in the following, as “treated” PMDI), in order to detect the different molecular weight fractions of the samples. Samples were dissolved in tetrahydrofuran (HPLC grade) at same concentration of 0.5% w/v and passed through a 0.22 μ m PTFE membrane filter. Measurements were performed on an injected volume of 100 μ L by using a Malvern - Viscotek GPC MAX/TDA 305 quadruple detector array equipped with a precolumn and two columns Phenogel Phenomenex with exclusion limits 10⁶ and 10³ respectively. The GPC instrument was used at flow rate of 0.8 mL min⁻¹ and at column and system temperature of 35 deg C. The samples were analyzed by using the universal calibration of polystyrene standards with peak molecular weight ranging between 500 Da and 1.8 10⁵ Da.

2.5. Spectroscopic analysis

Fourier Transform Infrared (FT-IR) spectroscopy in Attenuated Total Reflection (ATR) mode was conducted on the “as received” PMDI and on the extracted fluid contained in the CO₂-rich phase spilled from the pressure vessel, after CO₂ volatilization (addressed to, in the following, as “extracted” PMDI), in order to conduct a qualitative characterization to identify the chemical components of these samples. Nicolet 5700 FT-IR apparatus equipped with a Zinc Selenide (ZnSe) crystal was used to collect spectra, at room temperature, with a wavenumber resolution of 4 cm⁻¹, from 4000 to 500 cm⁻¹, for 32 scans.

3. Results and discussion

3.1. Sorption isotherm

Fig. 2 reports the sorption isotherm for the PMDI/CO₂ solution

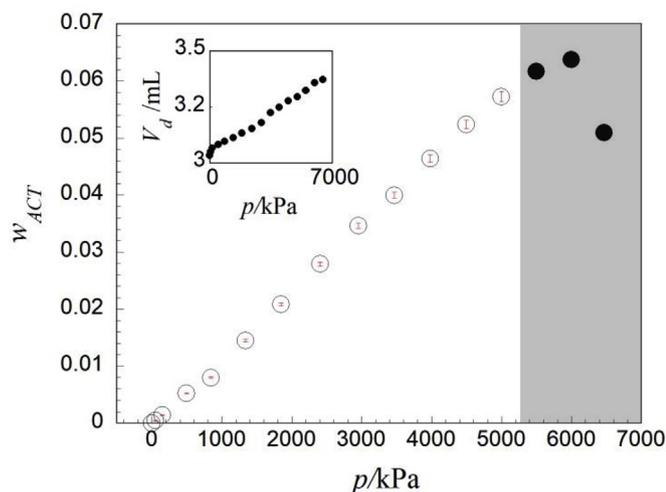


Fig. 2. Sorption isotherm of CO₂ in PMDI at 35 ± 0.1 deg C (in red, the error bars, calculated by accounting for the whole measurement chain). In the gray zone, closed symbols indicate erroneous solubility data, due to the partial extraction of PMDI by CO₂ at high pressures (see text for details). Inset: V_d vs. pressure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(calculated as by Eq. (3)), up to 6500 kPa and at a temperature of 35 deg C, showing a monotonic increase of the w_{ACT} as a function of pressure, up to a value of 6% ca. at a pressure of 5000 kPa (data are also reported in Table 2).

It is worth of note that, around 5000 kPa, a change in the trend of sorption isotherm was observed and, above 6500 kPa, a sharp w_{ACT} drop is evident. These outcomes point to the possible partition of PMDI between the condensed polymeric phase and the low-density gaseous phase at high pressures (referred to in the following as “PMDI extraction”), likely involving, preferentially, the low molecular weight fraction of PMDI sample. A similar behavior was already observed in the case of polyol-CO₂ system [3]. To verify this hypothesis, a further analysis was conducted by gravimetric tests in order to provide a quantitative estimate of the possible loss in weight of the PMDI rich phase due to PMDI partition. To this aim, 2 g of the “as received” PMDI, contained in a petri dish, were placed in a thermoregulated pressure vessel (0.3 L) which was then pressurized with CO₂ at 4500 or 5500 kPa and at 35 deg C for 24 h. The pressure was then released slowly enough to prevent foaming. PMDI was weighed before and after the treatment (i.e. after complete CO₂ de-sorption) in order to evaluate the possible loss in weight. No significant weight loss (<0.01%wt) was found at

Table 2
CO₂ solubility at different pressures and at $t = 35 \pm 0.1$ deg C.

p/kPa	w_{ACT}	uncertainty for w_{ACT} ^a
0	0	—
51.7	0.00042	3e-05
150.2	0.00139	4e-05
497.5	0.00522	9e-05
842.3	0.0080	1e-04
1339.3	0.0145	2e-04
1845.9	0.0209	3e-04
2406.9	0.0279	4e-04
2950.0	0.0346	4e-04
3466.8	0.0400	5e-04
3978.9	0.0464	6e-04
4496.9	0.0524	8e-04
4998.0	0.0573	9e-04

^a Calculated by accounting for the whole measurement chain.

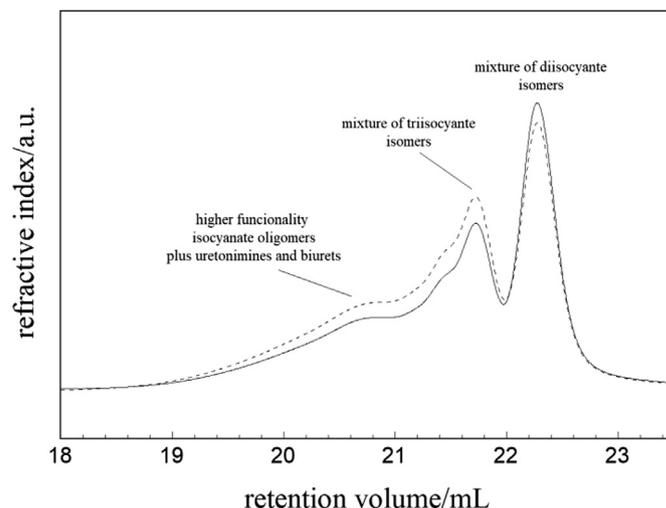


Fig. 3. GPC refractive index chromatograms of “as received” PMDI (solid line) and “treated” PMDI (dashed line).

4500 kPa, while at 5500 kPa (the first point that shows a deflection in the sorption isotherm in Fig. 2.) a loss of 0.3%wt was observed. GPC and FT-IR were utilized to gather further information on the extraction process by CO₂, performing analysis on the “as received” PMDI, on the PMDI after 24 h of contact with CO₂ at said conditions (referred to as “treated” PMDI) and on the small amount (of the order of a few mg) of PMDI “extracted” by CO₂, that was collected by precipitation on a filter during CO₂ evacuation.

3.1.1. GPC characterization

PMDI is a complex mixture of molecules. It contains both di-functional 4,4'-MDI and 2,4'-MDI, different grades displaying a different ratio of these two components. In addition, there are also higher molecular weight compounds, which are three functional and higher, each of which has multiples of isomers. Some of the molecules contain randomly distributed N-methyl carbamoyl chloride groups and other acidic impurity groups. Uretonimine, biuret or isocyanurate species are also present (see the main peak assignment in Fig. 3). All of these chemicals are difficult to be analytically separated and individually characterized. GPC is, however, capable of qualitatively characterizing PMDI, and baseline separation of di-, tri- and tetra-oligomers is also possible [1]. By comparing the GPC refractive index chromatograms of the “as received” and the “treated” PMDI (see Fig. 3, solid line and dashed line, respectively), it is possible to observe that in the “treated” PMDI some of the lower molecular weight fraction is missing, as compared to the case of the “as received” sample, thus indicating that part of the isocyanate-based material initially present in the crucible is likely extracted by CO₂, consistently with the sharp decrease in sorption evident in the isotherm reported in Fig. 2. In particular, we may speculate that the diisocyanate isomers, i.e. the lowest molecular weight components in the mixture, are the compounds that are prevalently extracted.

3.1.2. Spectroscopic characterization

PMDI samples have been analyzed by vibrational spectroscopy. In Fig. 4 are reported the FT-IR spectra of the “as received” PMDI (solid line) and of the “extracted” mixture (dotted line) contained in the CO₂-rich phase spilled from the pressure vessel, after CO₂ volatilization. It can be observed that both spectra present the main characteristic absorption band of PMDI at 2280 cm⁻¹ (NCO stretch) [22], thus confirming that part of PMDI was actually solubilized in

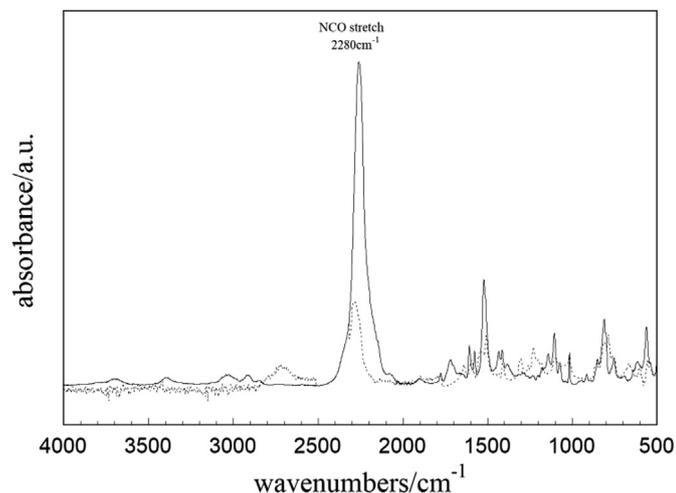


Fig. 4. FT-IR spectra of the “as received” (solid line) and the “extracted” PMDI (dotted line).

CO₂ at high pressures.

Although a quantitative estimate of partition of isocyanate-based compounds in the two phases at equilibrium was not possible, the analytical results evidence how a not negligible amount of components of the PMDI mixture is solubilized within the gaseous CO₂ rich phase. Experimental evidences indicate that this phenomenon is relevant at pressures above 5000 kPa. Based on these results, data collected above a pressure of 5000 kPa will not be further considered in the following, and only data collected in the 0–5000 kPa range will be discussed, assuming that PMDI doesn't solubilize within the external CO₂ gaseous phase.

3.2. CO₂/PMDI mutual diffusivity

Mutual diffusivity of the PMDI/CO₂ system has been investigated, determining the values of \bar{D} by fitting Fickian model (Eq. (5)) to sorption kinetics data. A very good fitting was always obtained confirming that the mass transport behavior is Fickian (see Fig. 5a) The calculated values for diffusivity are reported in Fig. 5b and in Table 3, as a function of average CO₂ mass fraction (\bar{w}_{ACT}). Again, for each sorption step we accounted for the increase of sample thickness, L , promoted by CO₂ sorption (swelling), by adopting in the fitting procedure of the sorption kinetics data a thickness value as evaluated by the arithmetic average of sample thickness at the start and at the end of the test. Values of sample thickness were retrieved from the value of volume of the PMDI/CO₂ as determined from drop volume measurement. In the investigated range of CO₂ pressure it was found that \bar{D} does exhibit a slightly increasing trend as a function of CO₂ concentration. This effect is related to the increase of free volume of the solution that promotes, in turn, an increase of the average mobility of the system and, hence, of the mutual diffusivity. No other data on similar (PMDI/CO₂) systems are available in the literature to perform a comparison.

3.3. Specific volume

Values of specific volume of PMDI/CO₂ solutions, in the investigated experimental range, have been calculated using Eq. (6). v_s data are represented in Fig. 6 and their numerical values are also reported in Table 4. It is evident that the specific volume markedly increases with gas pressure. This trend can be justified

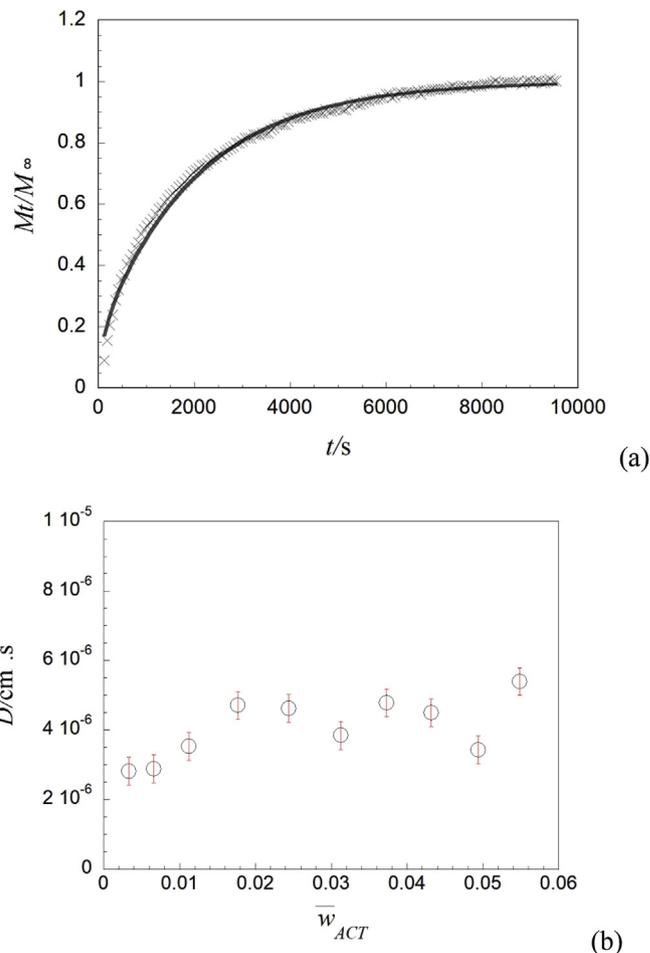


Fig. 5. (a) Typical transient sorption data (symbols), with the fitting line (see text for the details); (b) mutual diffusivity of CO₂ and PMDI at 35 ± 0.1 deg C (in red, the error bars, calculated by accounting for the whole measurement chain). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

by considering that, when a polymer is exposed to a high-pressure gas, two mechanisms compete in affecting the value of specific volume of the PMDI/CO₂ mixture: (i) mechanical action of pressure exerted by the external gas promotes a compression of the gas-saturated polymer and, thus, a reduction of specific volume as the pressure increases; (ii) solubilization of carbon dioxide molecules promotes an increase of specific volume as pressure increases in view of the higher free volume associated to condensed

Table 3

Mutual diffusivity at different average CO₂ mass fraction and at $t = 35 \pm 0.1$ deg C.

\bar{w}_{ACT}	$\bar{D}/\text{cm}^2\cdot\text{s}^{-1}$
0.00330	2.8e-06
0.0066	2.9e-06
0.0112	3.5e-06
0.0177	4.7e-06
0.0244	4.6e-06
0.0313	3.8e-06
0.0373	4.7e-06
0.0432	4.4e-06
0.0494	3.4e-06
0.055	5.4e-06

Uncertainty is 5e-07 cm² s⁻¹ for \bar{D} , calculated by accounting for the whole measurement chain.

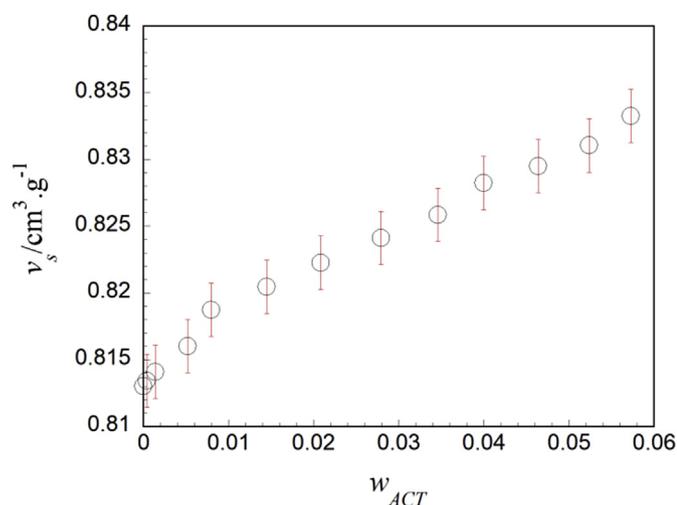


Fig. 6. Specific volume of PMDI/CO₂ solutions at 35 ± 0.1 deg C (in red, the error bars, calculated by accounting for the whole measurement chain). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

carbon dioxide as compared to PMDI. In the case at hand, v_s is monotonically increasing with gas pressure, proving that the prevailing effect is that associated to the gas solubilization.

3.4. Interfacial tension of the PMDI/CO₂ solution in contact with CO₂

Another property relevant for engineering applications is the interfacial tension, γ , of the PMDI/CO₂ solution in contact with gaseous CO₂. In Fig. 7 is reported the effect of CO₂ concentration on γ . In the selected experimental range, interfacial tension of the PMDI decreases with the CO₂ pressure (numerical values are also reported in Table 5), with a drop from 36.3 mN m⁻¹ for the neat MDI to 15.4 mN m⁻¹ for the PMDI/CO₂ solution with 5.7% CO₂ at 5000 kPa. Such a decrease in the interfacial tension with the gas concentration has already been reported elsewhere [23–27] and is generally attributed to two concurrent phenomena [26,27]: (i) as pressure increases, the free energy density of CO₂ becomes closer to that of the polymer phase and the interfacial tension decreases; (ii) as gas pressure increases, the concentration of CO₂ in the polymer phase increases thus further promoting a decrease of interfacial tension since the two phases in contact become more

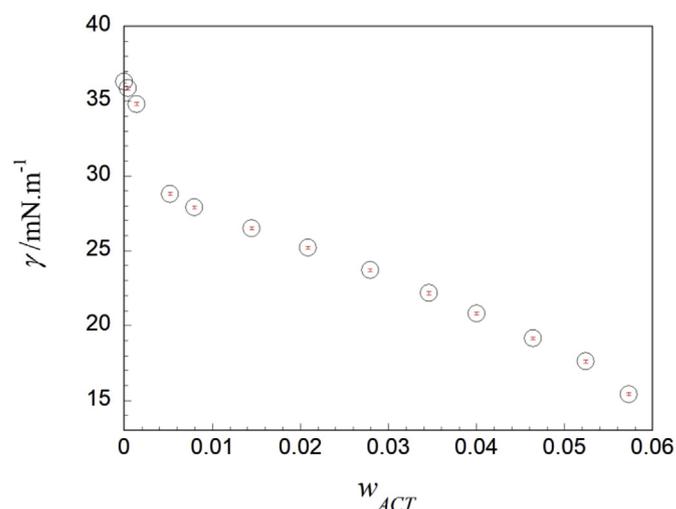


Fig. 7. Interfacial tension between PMDI/CO₂ solutions and CO₂ at 35 ± 0.1 deg C (in red, the error bars, calculated by accounting for the whole measurement chain). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

similar. Another possible cause for the observed decrease of interfacial tension could be the change in acidity of PMDI promoted by dissolved carbon dioxide. Actually, in the investigated system, neat PMDI shows a non-negligible acidity (as measured in terms of equivalent HCl%, see Table 1), which possibly changes as a consequence of CO₂ sorption when pressure increases. In fact, such an acidity increase has been observed in the case of aqueous solutions and acid-catalyzed isobutane–isobutylene alkylation with CO₂ [28,29]. Moreover, this acidity change has been reported to effectively modify the value of γ in several cases, as for aqueous solutions of sodium oleate [30] and of crude oils [31]. Nevertheless, we do not have access to experimental values of acidity of PMDI/CO₂ solutions as a function of CO₂ pressure and, consequently, although we cannot rule out this effect in the case at hand, we do not have at the moment any evidence that the observed decrease of interfacial tension is promoted by a decrease of pH associated to CO₂ sorption.

A common way to elaborate interfacial tension data is based on Macleod's relation (see Eq. (7)), in which γ is reported as function of the density difference between the high density and the low-density phases (in our case the PMDI/CO₂ solution and the CO₂, respectively):

Table 4
Specific volumes at different CO₂ mass fraction and at $t = 35 \pm 0.1$ deg C.

w_{ACT}	$v_s/\text{cm}^3 \cdot \text{g}^{-1}$
0	0.813
0.00042	0.813
0.00139	0.814
0.00522	0.816
0.0080	0.819
0.0145	0.820
0.0209	0.822
0.0279	0.824
0.0346	0.826
0.0400	0.828
0.0464	0.829
0.0524	0.831
0.0573	0.833

Uncertainty is 0.2% for v_s calculated by accounting for the whole measurement chain.

Table 5
Interfacial tension at different CO₂ mass fraction and at $t = 35 \pm 0.1$ deg C.

w_{ACT}	$\gamma/\text{mN} \cdot \text{m}^{-1}$
0	36.3
0.00042	35.9
0.00139	34.8
0.00522	28.8
0.0080	27.9
0.0145	26.5
0.0209	25.2
0.0279	23.7
0.0346	22.2
0.0400	20.8
0.0464	19.1
0.0524	17.6
0.0573	15.4

Uncertainty is 0.1 mN m⁻¹ for γ , calculated by accounting for the whole measurement chain.

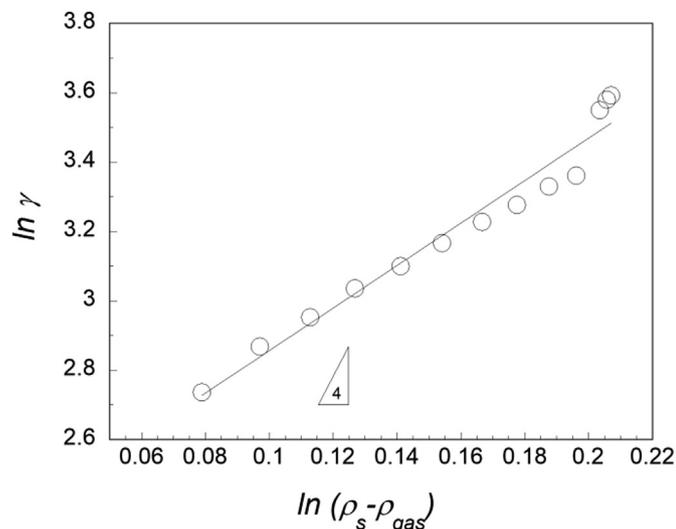


Fig. 8. Macleod plot for the PMDI/CO₂ solution (fitting with Eq. (7)).

$$\gamma = C(\rho_s - \rho_{gas})^n \quad (7)$$

where C is a characteristic constant for a given fluid, $\rho_s = 1/v_s$ is the density of the PMDI/CO₂ solution, and n is the Macleod's exponent. The exponent n is close to 4 for many unassociated liquids of low-molecular-weight substances [32]. In our case values of 10 and 5.2 were respectively estimated for C and n (see Fig. 8).

According to Sugden's equation (Eq. (8)) [33], from C it is possible to calculate the parachor (P), an empirical constant that relates γ to the molecular volume:

$$P = C^{1/n} M = \frac{M}{\rho_s - \rho_{gas}} \gamma^{1/n}, \quad (8)$$

where M is the molecular weight of the fluid. The quantity $M/(\rho_s - \rho_{gas})$ has the dimensions of a volume and at low temperatures, where ρ_{gas} becomes very small, it represents the molar volume of PMDI. In our case, the theoretical value for M (as calculated according to [1]) is 365 Da, from which a value of parachor $P = 565 \text{ (cm}^3 \cdot \text{mol}^{-1}) \cdot (\text{mN} \cdot \text{m}^{-1})^{1/5.2}$ is obtained (use, instead, of $n = 4$ gives as estimate for $P = 649 \text{ (cm}^3 \cdot \text{mol}^{-1}) \cdot (\text{mN} \cdot \text{m}^{-1})^{1/4}$).

The values of γ can be also correlated to CO₂ concentration by using the following empirical equation [34]:

$$\gamma = (1 - w_{ACT}) \gamma_{PMDI}^{1/r} \quad (9)$$

where γ_{PMDI} is the surface tension of the "as received" PMDI at 0 kPa. From the fitting of the experimental data (not shown), the parameter r was estimated to be equal to 1.02.

4. Conclusions

Solubility, mutual diffusivity, specific volume and interfacial tension of PMDI/CO₂ solutions were measured at 35 deg C and at pressures up to 6500 kPa by using a fully-experimental, coupled gravimetry-Axisymmetric Drop Shape Analysis. Examination of data was performed only up to 5000 kPa, since gravimetry, GPC and vibrational spectroscopy indicate that significant solubilization of PMDI within the gaseous CO₂ phase occurs at higher pressures.

In the investigated experimental range, the sorption isotherm for the PMDI/CO₂ solution shows a monotonic increase of the ω_{ACT}

as a function of pressure, up to a value equal to 6% ca. at a pressure of 5000 kPa, while mutual diffusivity slightly increases with CO₂ concentration. Furthermore, interfacial tension of the PMDI decreases with the CO₂ pressure, reaching the value of 15 mN m⁻¹ ca. at 5000 kPa, while specific volume increases with increasing CO₂ concentration. Finally, GPC and FT-IR characterizations reveal that some lower molecular weight fractions of PMDI, possibly diisocyanate isomers, are extracted by CO₂ at high pressures.

Acknowledgment

The authors are grateful to Prof. Giuseppina Luciani and Dr. Giuseppe Vitiello (Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, University of Naples Federico II) for FT-IR spectroscopic analysis.

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