

Property Data and Phase Equilibria for the Design of Chemical Processes involving Carbon Dioxide

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Thesis to obtain a Master degree in

Chemical Engineering

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October 2017

Acknowledgements

I would like to express my sincere appreciation to everyone who assisted me, in one way or another, to complete this thesis.

First of all I would like to thank Prof. Eduardo Filipe for getting me involved with this project in partnership with such a great company like Covestro Deutschland AG, also for his support, knowledge, insights and guidance throughout the writing.

Then, I would like to show my deepest appreciation to Dr. José Fonseca for welcoming me in the group, for his unconditional orientation, constant help and for thermodynamics expertise and experience in equipment design and preparation. I also want to thank the rest of the team of the Thermodynamic group, especially to Stefan David for the constant support in the lab, to Hans-Gerd for all the experience in many fields and to Mr. Tobias Grömping for keeping me in track with the company and team in the scientific and burocratic field. These months in Covestro were undoubtedly the highlights of my university course for what I've learned not only in the scientific field but also in the enterprise world.

And the last but not the least, I want to thank all my family, and closest friends, especially my parents and Matilde Leitão for the never ending belief, constant support, and encouraging attitude not only during my internship and thesis but always.

Resumo

Este trabalho está dividido em duas partes. O primeiro é focado no equilíbrio de fases para design de processo e compreende a medição da solubilidade do Azoto (N_2) em 2 monómeros importantes na produção de um polímero inovador, 1,4-butanediol and hexamethyl diisocyanate (HDI). As medições foram feitas a temperaturas de 303 K e 313 K de aproximadamente vácuo até 8 bar. Para a otimização do processo de produção do Cardyon™, um polímero inovador que utiliza dióxido de carbono (CO_2) como matéria-prima, foi medida a solubilidade de CO_2 em 2 policarbonatos diferentes a temperaturas de 353 K e 383 K com pressões até 75 bar.

A segunda parte do trabalho centra-se na determinação de propriedades físicas, nomeadamente as viscosidades e as capacidades caloríficas das misturas binárias, 1-Butanol (But) + 1H, 1H-Heptafluorobutanol (PFB) e 1-Hexanol (Hex) + 1H, 1H-Undecafluorohexanol (PFH), em toda a gama de composição. As viscosidades foram determinadas a temperaturas de 283 K até 313 K para But + PFB e de 283 K até 353 K para Hex + PFH, respectivamente. As capacidades caloríficas foram estudadas a temperaturas de 295 K até 330 K para But + PFB e de 305 K até 330 K para Hex + PFH, respectivamente. As propriedades de excesso correspondentes foram determinadas e estudadas.

Abstract

This work is divided in two parts. The first is focused on phase equilibria for process design and comprise the measurement of the solubility of nitrogen (N_2) in 2 important monomers being used in the production of an innovative polymer, 1,4-butanediol and hexamethyl diisocyanate (HDI). This was done at temperatures of 303 K and 313 K from nearly vacuum up to 8 bar. For the optimization of production process of Cardyon™, an innovative polymer using carbon dioxide (CO_2) as raw material, the solubility of CO_2 in 2 different polycarbonates was measured at temperatures of 353 K and 383 K at pressures up to 75 bar.

A second part of the work focused on the determination of physical properties, namely the viscosities and heat capacities of the binary mixtures, 1-Butanol (But) + 1H,1H – Heptafluorobutanol (PFB) and 1-Hexanol (Hex) + 1H,1H – Undecafluorohexanol (PFH), in its entire composition range. Viscosities were studied at temperatures from 283 K up to 313 K for But+PFB and from 283 K up to 353 K for Hex+PFH respectively. Heat capacities were studied at temperatures from 295 K up to 330 K for But+PFB and from 305 K up to 330 K for Hex+PFH respectively. The correspondent excess properties were determined.

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1. Introduction

Carbon dioxide (CO₂) currently is and has been for a several years a major concern in terms of greenhouse gases emissions. On the other hand, nowadays more than half a million tons of crude oil is processed for the production of polymers every day (1). The targets for the reduction of greenhouse gas emissions and of energy consumption in the chemical industry were set high, with companies investing in ambitious environmental programs which often require the development of innovative products and processes (2).

For this matter the chemical transformation of carbon dioxide to produce high-value chemicals and materials in a sustainable manner is currently attracting great interest and is for sure a topic of growing relevance. The motivation for utilizing CO₂ on an industrial scale basically emerges from: achieving sustainability through substituting fossil feedstock, reducing the carbon footprint of processes and products by preventing the release of CO₂ plus fixing CO₂ for long duration periods and generating added value by establishing innovative processes based on CO₂ as abundant, low-cost and non-toxic carbon source (3).

The direct chemical application of CO₂ as a co-monomer in polymerization reactions to yield tailor-made materials seems to be a particularly promising approach (4). This highly innovative project ran by Covestro AG consists in using CO₂ as a raw material for the production of high quality polyurethanes which find wide application in, for example, rigid and flexible foams, adhesives, and many other materials, thus being a multi-million industry (Figure 1) (2).

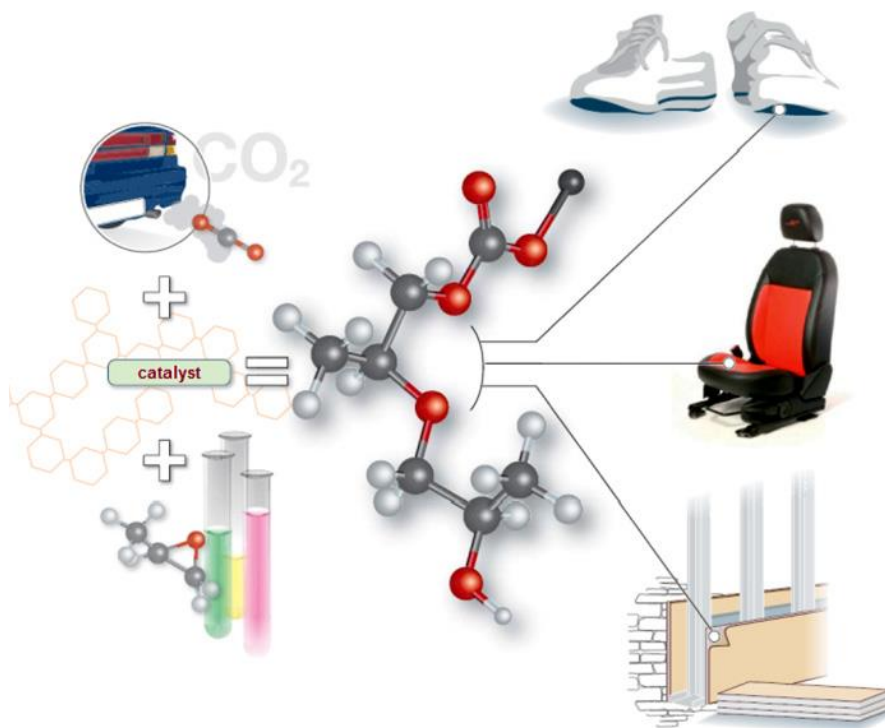


Figure 1 - Illustration of the use of CO₂ as a raw material in the production of polyurethanes used for diverse industries. Courtesy of Bayer AG (1).

Basically these innovative polymers are Polyether Polycarbonate Polyols (named as PET-CO₂ in this dissertation) and are the precursors used in the production of polyurethanes. They are produced by the catalytic ring opening polymerization of propylene oxide (PO) and/or ethylene oxide (EO) with CO₂ in the presence of multifunctional alcoholic “starters” (5) (Figure 2). Apart from the savings of the production of one of the monomers, the CO₂ balance is improved by directly using this gas from power plants (6).

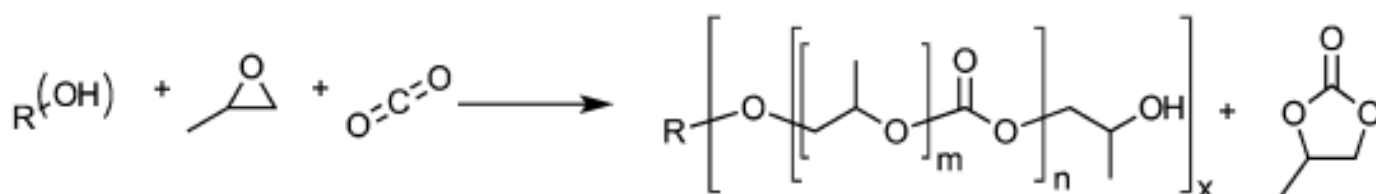


Figure 2 - Representation of the general chemical reaction for the production of Polyether Polycarbonate Polyols.

The use of CO₂ as a raw material in the production of polymers had being considered for a long time, but the reaction of CO₂ revealed to be extremely unfavorable from the energetic point of view. These thermodynamic limitations were overcome with the use of high energetic monomers like epoxides in combination with the development of appropriate catalysts. In addition, to fight these energetic drawbacks, there were developed some concepts based on the transformation of CO₂, for example, with regenerative hydrogen to other C₁ building blocks (formaldehyde, formic acid, methanol, etc.) (5).

On top of this, the properties of these new polymers can be adjusted in a wide range by tuning the CO₂ amount and architecture. The feasibility of using such tailored polymers in the production of polyurethanes is demonstrated as a great example for a novel CO₂ utilization with huge industrial potential and nowadays a pilot plant is already built and successfully producing high quality polymers with an incorporation of CO₂ above 20%wt (4)

a) Phase Equilibria in process design and optimization

Knowledge of phase equilibria is and has been for long time now crucial in many fields, from the scientific understanding of natural processes to the optimization of industrial processes that results in lower manufacturing costs. Besides, high-pressure phase equilibria today is essential for the design of new environmentally friendly, compatible and profitable processes for many health, safety, environment and quality issues (7).

In the chemical industry, pressure is one of the state variables that are determinant in any thermodynamic equilibrium because it strongly influences the composition of the coexisting phases. A pressure increase may not only induce a phase transition, e.g. from vapor to liquid or from liquid to solid, but can also force gas dissolving in liquid phases resulting in substantial changes in their physical properties and chemical potential (7).

Nowadays the knowledge of pressure effects on phase equilibria is fundamental for the design and optimization of high-pressure chemical and separation processes such as high-pressure reactions, supercritical fluid applications and gas and polymer processing (8). Even though computational methods for data prediction and process simulation have made considerable progresses in the past decades in several areas, the experimental determination of phase equilibria or thermodynamic property data (in this case) remains an indispensable source of data. On top of that, at high pressures and/or high temperatures the phase behavior is more complex than at ambient conditions and for that reason thermodynamic models are less precise and combination with experimental data becomes an important need on this field. It is true that experimental determinations may be difficult and expensive but it is very often more expensive, for a company, to use imprecise or estimated data over the years (7).

Several other areas such as petroleum reservoir simulation, enhanced oil recovery, carbon capture and storage, transportation and storage of natural gas, refrigeration and heat-pump cycles, applications of ionic liquids and other geological processes are also dependent of high-pressure phase equilibrium data (1)

As aforementioned, experimental research had a huge role in the high-pressure phase equilibria subject through the years, and nowadays several methods and techniques are currently available for experimental studies. Every method is appropriate for its own kind of phenomena, depending on the physical properties and on components behavior, meaning that every case is treated individually. Of course, every method has its own advantages, disadvantages as well as error sources, and for that reason a deep knowledge and understanding of every single method is a main concern for the validation of experimental data (7) In this work, it was studied phase equilibria at high pressures, and for that reason the synthetic-isothermal method, according to the classification proposed by Dohrn et al (7) is particularly suitable.

b) Fluorinated Compounds

The abnormal behavior of solutions of fluorinated compounds was discovered in the 1950's through a wide investigation of properties such as heat of mixing, vapor pressures, solubilities, and volume changes of mixing by Scott (9). A renewed interest in fluorinated compounds arised in the last years due to the great potential they have either for industrial or biomedical applications (10). Moreover, the solubility of simple gases in fluorinated carbons have been proved to be higher than in the regular hydrogenated carbons, and for this reason, fluorinated compounds and its mixtures, have to be considered as another potential environmental friendly method for capturing and using carbon dioxide. (11) (12)

This recent grow of fluorocarbons importance and presence in industrial applications resulted in an increase of interest in physical, chemical and thermodynamic properties of these compounds and their mixtures. From the experimental point of view, thermodynamic properties such as excess enthalpies, excess molar volumes, etc, provide valuable information when analyzing and understanding structural formations, different kinds of associations, and various types of intermolecular interactions.

Mixing two or more liquids leads to deviations in physical, chemical and thermodynamic properties due to changes in free volume, energy, and molecular orientation and differences in the molecular size, shape, structure and the extension of solution theories because they depend on solute– solute, solvent–solvent and solute–solvent interactions and the structural effects arising from interstitial accommodation (13). These new molecular interactions along with new hydrogen-bonding bring attached several advantages. Binary and Ternary mixtures provide unique qualities of each component. The combination of compounds widely extends the possibilities of properties when comparing to the use of single components systems. Since there is not a chemical reaction, the chemical properties stay the same making possible to tune physical and thermodynamic properties into adequate values resulting in highly effective new compounds (14).

The deviation from ideality is expressed by many thermodynamic properties, especially in terms of excess thermodynamic properties, that correspond to the difference between the measured property and the value if the system behaved ideally. These properties are generally convenient parameters for interpreting and explaining the interactions of these liquid mixtures in solution, which is the ultimate goal of thermodynamics. Studies of excess properties are essential in many industrial applications such as heat transfer, design calculations, mass transfer, fluid flow, etc (13).

This work includes the study of mixtures containing fluorotelomer alcohols which are highly fluorinated molecules with a functional head, in this case a alcoholic group -OH with a general formula $CF_3(CF_2)_n(CH_2)_mOH$ (in this work $n = 2, 3$ & $m = 1$). These fluorinated alcohols have commercial value in several fields from textile protection agents and fire-fighting foams, to detergents, paints, and as precursors in the production of fluorinated polymers (15).

i. Viscosity

Although there is plenty of thermodynamic and transport data of binary mixed solvents, investigations of the properties of mixtures containing fluorinated compounds, over a temperature or composition range are still very scarce in the literature. In this work we have studied the viscosity of 2 mixtures containing fluorinated alcohols (C4 and C6) and their respective hydrogenated equivalent, for both of which there is no data in the literature. Data for alkane + perfluoroalkane mixtures can be found in literature which can be useful in the understanding of the behavior of perfluoroalkanol + alkanol mixtures.

It is well known that compounds containing hydrogenated and fluorinated chains, despite having similarities in their components, show enhanced tendency to phase separation, which is supported by extensive deviations from ideal behavior such as liquid-liquid immiscibility, large positive excess volumes and enthalpies, positive deviations to Raoult's law, between others (16).

It is also known that unlike many other immiscibility cases, the segregation of fluorocarbons and hydrocarbons is a combination of relatively weak dispersion forces such as the big difference between molecular cross-sectional diameters and the opposite structural behavior of chains, since fluorocarbons chains are very rigid (due to fluorinated atom size) and hydrocarbons chains are very flexible (11).

Studies of perfluoroalkanol + alkanol mixtures bring the introduction of a form of association on top of the presence of mutually phobic segments (hydrogenated and fluorinated chains) which is hoped to help to understand the liquid structure and molecular organization (16).

The addition of polar alcoholic group at the end of each chain, as it is well known, will induce the formation of hydrogen bonds that can be seen as on-off associate interactions between the two phobic components. These hydrogen bonds will give rise to relatively large and flexible chains based on hydrogen bonds zigzagging throughout the alcoholic bulk, storing the phobic chains in the best possible way. These alcoholic chains can be either linear or cyclic and its average length can vary considerably. This results in an organized microheterogeneous structure that reflects the balance between optimizing the H-bonds and packing the carbon chains which are governed by dispersive and repulsive interactions (16).

One of the obstacles in 'packing' efficiently these apolar segments is the chain stiffness in fluorocarbons which result in the existence of free spaces in the liquid. This can explain, in part, the enhanced solubility of simple gases in liquid perfluoroalkanes (11).

ii. Heat capacities

The specific heat capacity is a very important thermodynamic property since it provides information about the energy that can be stored in a system. When appropriate model are used, it allows an analysis on a molecular level (17).

This thermodynamic property is critical in engineering specially when designing systems where the management of heat is essential, including refrigeration and / or heating systems and of course, almost all electronics where the management of waste heat is critical (18). It is a very crucial property in the design of heat exchangers, the dimensioning of heat sinks and in any energetic optimization of a plant. However, since heat capacity at a constant pressure is a property related to the second derivative of the chemical potential with respect to the temperature, it is very sensitive to any structural changes that may occur in the system.

Measurements of specific heat capacities at a range of temperatures can be used to determine energy balances and estimate derivative properties such as enthalpy (H), entropy (S) and Gibbs energy (G). Excess heat capacities may be useful in the developing of theoretical models and also in designing suitable mixed solvents for several industrial processes (17).

Even though there are some excess heat capacities studies of alcohols in the literature, only few results are available for mixture of alcohols, and nearly none for fluorinated alcohols. It was shown by Yao (19) through measurements of excess enthalpy for several pairs of primary alcohols that excess heat capacities for mixtures of primary alcohols are negative, increasing very little in magnitude with the chain length. Yao also studied the excess specific heat capacity of a mixture of a primary with a tertiary alcohol where the degree of hindrance in the neighborhood of the hydroxyl is different. It was discovered that this mixture has an S-shaped behavior, having a negative deviation to ideality at low concentration of tertiary alcohol and a positive deviation at high concentrations. These negative deviations indicate weaker interactions between the molecules in solution.

Lepori et al. (10) studied the excess enthalpy (HE) of several mixtures of alkane + perfluoroalkane of F6 + H_n and H6 + F_n with *n* from 5 to 8, obtaining positive deviations to ideality and increasing values with *n*. The same authors also estimated CpE of these mixtures, measuring HE's at two different temperatures obtaining positive values, which could not be explained, since they mean it is needed more energy to heat the same quantity of substance, which in turn indicates stronger intermolecular interactions, counteracting everything that has been studying so far with mixtures containing hydrogenated and fluorinated chains.

In this work we have determined and studied the excess enthalpy of 2 different alkanol + perfluoroalkanol systems (C4 and C6). It is believed these are the first studies of this property for these pairs.

2. Experimental Techniques

a) Phase Equilibria

In this work the gas-liquid solubility of nitrogen (N_2) and carbon dioxide (CO_2) were measured in different solvents at pressures up to 8 bar and 75 bar, respectively, using the synthetic-isothermal method described in detail by Dohrn et al. (7). The equilibrium cell is immersed in a thermal bath (*Lauda Proline PV 24*), with temperature precision of $\pm 0,01K$. The temperature inside the cell is determined with high precision by a platinum resistance thermometer (Pt100), previously calibrated and tested, with stability of $\pm 0,1K$. The pressure inside the cell is determined by a high-precision transducer Keller PAA-33X with a range of 10 and 100 bar with an accuracy of 0.1% of full scale. The homogeneity is guaranteed by a centrifugal stirrer Premex MINI 100, all made in stainless steel, with some customized details to this specific kind of measurements. The whole procedure is based on pressure measurements and for this reason the cell is previously isolated to prevent the minimal leak and the pressure sensors are carefully calibrated before and between every measurement.

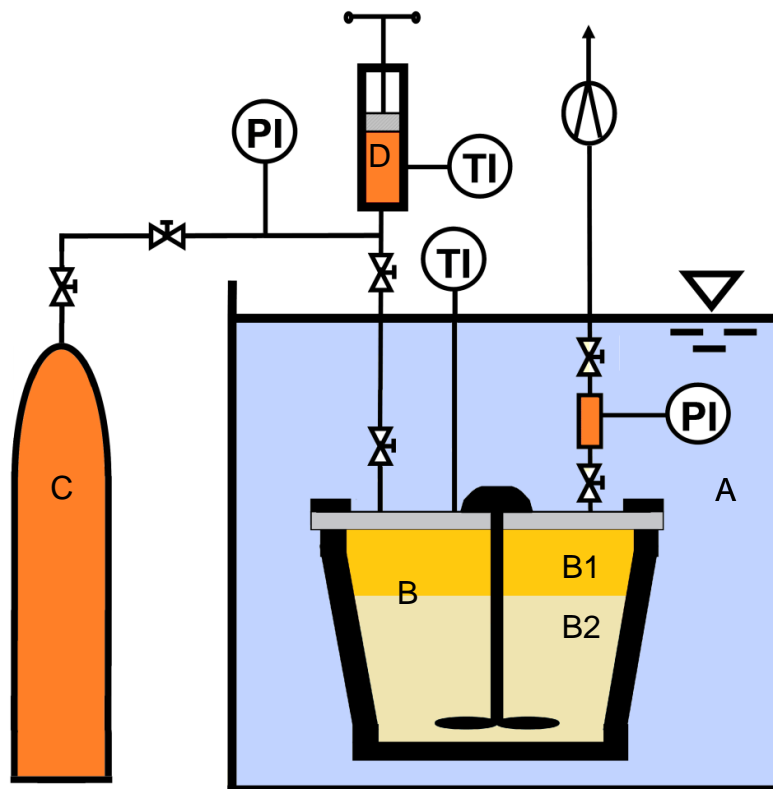

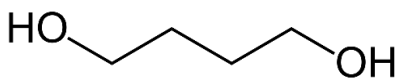
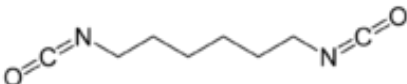


Figure 3 - Experimental apparatus of high-pressure Fluid Phase Equilibria. (A- Thermal Bath; B- Equilibrium Cell; B1- Volatile Phase; B2- Condensed Phase; C- Gas Bottle; D- Injection Pump; TI- Temperature Transducer; PI- Pressure Transducer.

i. Solubilities of N₂

The solubility of Nitrogen (N₂) was measured in 1,4-butanediol and HDI at pressures up to 8 bar and at temperatures of 303 and 313 K. Molecular structures, the manufacturer and other important properties of the monomers mentioned are presented in Table 1. In these experiments a full stainless-steel equilibrium cell was used, with an operating pressure range up to 40 bar, immersed in a thermal bath containing water as thermal fluid. The injection of the nitrogen is made through a pump that is also immersed on the bath. The pressure inside the pump is also determined by a high-precision transducer Keller PAA-33X with the stability of $\pm 0,001$ bar and an accuracy of 0,05 % FS.

Table 1 - Molecular structure, manufacturer and relevant properties of 1,4-butanediol and HDI. Properties from: 1- Aldrich Chemical Company; 2- Cameo Chemicals; 3- WorldCat data base; 4- NIOSH Guide to Chemical Hazards.

Compound Name	Molecular Structure	Manufacturer (Purity)	Boiling Point (at P=1bar)	Vapor Pressure (at T=25°C)
Nitrogen		Linde (>0.99999)	---	---
1,4-butanediol		Merck (>0.99)	503.2 K ⁽¹⁾	0.0105 mmHg ⁽³⁾
HDI		Produced by Covestro AG in a pilot plant in Leverkusen, Germany.	528.2 K ⁽²⁾	0.050 mmHg ⁽⁴⁾

Experimental Procedure

A precisely weighted (± 0.001 g) sample is introduced in a previously evacuated equilibrium cell, and then it is degassed until the cell pressure matches the vapor pressure of the liquid phase, under the desired experimental conditions. With the sample degassed, exactly known volumes of the volatile component, in this case N₂, are injected step by step in the cell. It is considered that N₂ behaves as an ideal gas and quantity injected is determined by the pressure variation (± 0.001 bar) in a pump with precisely known volume and temperature (immersed in the thermal bath). In every step, once the equilibrium is achieved, the composition of the volatile component on the liquid phase is calculated through a mass balance that is described next.

With the pressure variation of the pump in combination with a reference equation of state (20) it is precisely calculated the injected mass of N₂ in the cell. After that, as a first iteration it is considered that the volume of the liquid phase does not vary with the amount of gas solubilized, which is not far from reality when low solubilities are considered as in the current case. The phase volumes are known since the liquid phase volume is exactly the volume of the sample previously introduced, of which the density is known. The amount of N₂ in the gas phase is calculated through the density at the respective pressure and temperature conditions, using a reference equation of state. Here it is assumed that the gas phase is consists exclusively of N₂ given the low volatility of the solvent. The amount of dissolved N₂ is then calculated from the difference between the gas injected and that on the gas phase at equilibrium. The density of the liquid phase can then be calculated considering the determined amount of gas dissolved in this phase, considering an ideal mixture (excess volumes = 0). This iterative process is repeated until the variation in the solubility values is insignificant. A simulation of the iterative process is represented on the scheme on the Figure 4.

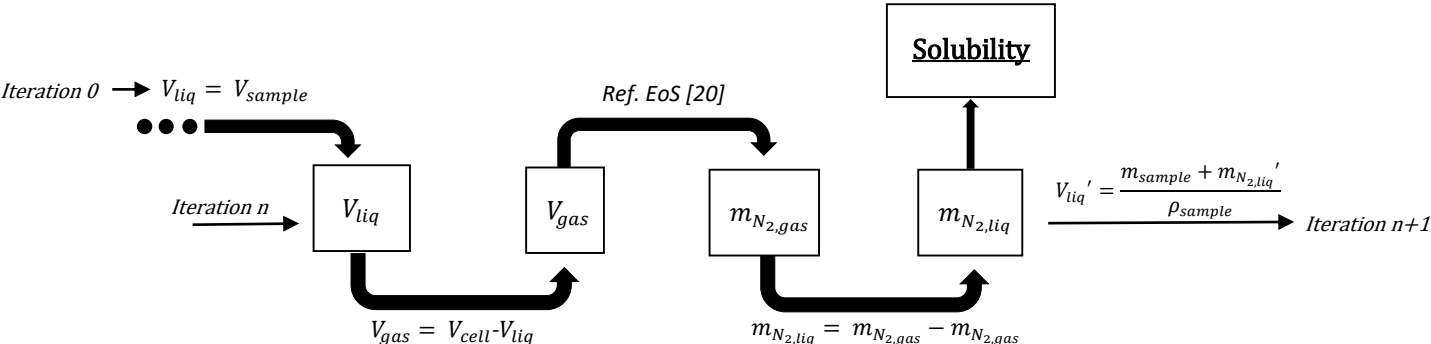


Figure 4 - Systematization of the iterative process used to calculate solubilities.

ii. Solubility of CO₂

The solubility of CO₂ was measured in two different types of PET-CO₂ polymers, named by Type5C and Type10C, at pressures up to 70 bar at temperatures of 353 K and 393 K. The exact structure of the polymers cannot be published, but the basic molecular structure of these polymers and some overall properties, such as hydroxyl number, molar mass average (Mn) and amount of CO₂ in structure, are represented in the table 2. It was used a cylindrical cell with a 360° sapphire glass window immersed in a thermal bath. The chosen thermal fluid was *polyethylene glycol*.

Table 2 - Identification, structure and some properties of both PET-CO₂ polymers studied.

Compound	Molecular Structure	Manufacturer (Purity)	Name	Hydroxyl Number	Mn [g/mol]	CO ₂ [wt%]
Carbon Dioxide	<chem>O=C=O</chem>	Linde (0.99995)	----	-----	-----	-----
Polyether Polycarbonate Polyols (PET-CO ₂)		Internal Product	Type 5C	56.4	1989	18
		Internal Product	Type 10C	56.2	2795	20

Experimental Procedure

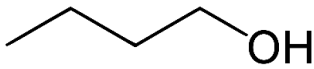
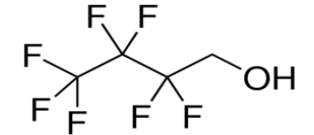
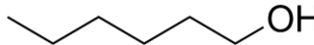
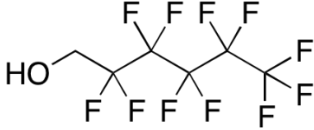
A precisely weighted (± 0.001 g) sample is introduced in a previously evacuated equilibrium cell (Figure 3 - B), and then it is degassed until the cell pressure matches the vapor pressure of the liquid phase, under the desired experimental conditions. The gas to be injected, CO₂, is kept at low temperature, far from its critical temperature around which the uncertainty in the temperature would have a larger impact on the density. CO₂ was kept at 100 bar in the syringe pump (represented as D in Figure 3) and at 283 K by a thermostat circulating cold water. The exact volume of each injection is accurately determined by the round counting of the syringe. The precise amount of CO₂ injected is calculated from the injected volume through a reference equation of state, in the case of CO₂ the equation proposed by Span and Wagner (1996) was used (21). The composition of the volatile component on the liquid phase is calculated through a mass balance as described in the previous section..

The volume of the liquid phase was calculating based on the information from previous experiments (2), where it was observed that the volume of the liquid phase increased 1.5 % for every 1 wt% of CO₂ dissolved.

b) Physical Properties

The viscosity and heat capacity studies were performed for 2 binary mixtures, both composed by a hydrogenated and a fluorinated alcohol. The studied pairs were *1-butanol + heptafluoro-butanol* (But + PFB) and *1-hexanol + undecafluoro-hexanol* (Hex+PFH), represented in the table 3 along with its molecular structure, product manufacturer and boiling point. The mixtures were prepared through mass weighing with precision of ± 0.01 g. Alcohols are hygroscopic, and so they were previously dried with molecular sieves and every sample were prepared in a glove box, under Nitrogen atmosphere.

Table 3 - Molecular Structure, manufacturer and boiling point of the studied compounds.

Pair #	Chemical	Molecular Structure	Manufacturer (Purity)	Boiling Point (at 760mmHg)
1	1-Butanol (But)		<i>Sigma Aldrich</i> (≥ 0.99)	390.9 K
	Heptafluorobutan-1-ol (PFB)		<i>Sigma Aldrich</i> (≥ 0.98)	368.0 K
2	1-Hexanol (Hex)		<i>Sigma Aldrich</i> (≥ 0.99)	429.0 – 430.0 K
	Undecafluorohexan-1-ol (PFH)		<i>ABCR</i> (≥ 0.98)	403.0 – 404.0 K

i. Viscosity

The viscosity were measured using a Stabinger SVM 3000 G2 manufactured by Anton Paar, Austria, with a precision of ± 0.0001 mPa.s. It was used a temperature scanning method from 283 K up to 50 K below the lowest boiling point of each pair (323 K and 353 K respectively), with 10K steps. It was made enough measurements to get 3 concordant values for each point. The equipment was previously tested, using several reference substances, provided by the manufacturer with a very high concordance.

ii. Heat Capacities

The specific heat capacity was measured at temperatures from 293 and 303 K up to 50 K below the lowest boiling point of each pair, 323 K for that with butanol and 353 K for the mixture with hexanol. The equipments used for the determination of this thermal property were two Setaram C80 Calvet-type calorimeter, manufactured by Setaram instrumentation, France with an enthalpy accuracy of $\pm 1\%$. The C_p were measured using a step method, using temperature steps of 10 K with 2 hours of stabilization in between. The results were calculated with the software provided with the equipment by direct integration of the enthalpy peaks. The cells used were made of hastelloy, with a volume disperser, specially designed for liquid C_p measurements. The calibration of this apparatus is verified regularly with high-purity reference substances such as Indium or Tin with mass fractions higher than 0.99999 or Gallium (mass fraction higher than 0.999995). Tests with benzoic acid confirmed the validity of the calibration, with discrepancies lower than 1 % when comparing the results with literature (Figure 5).

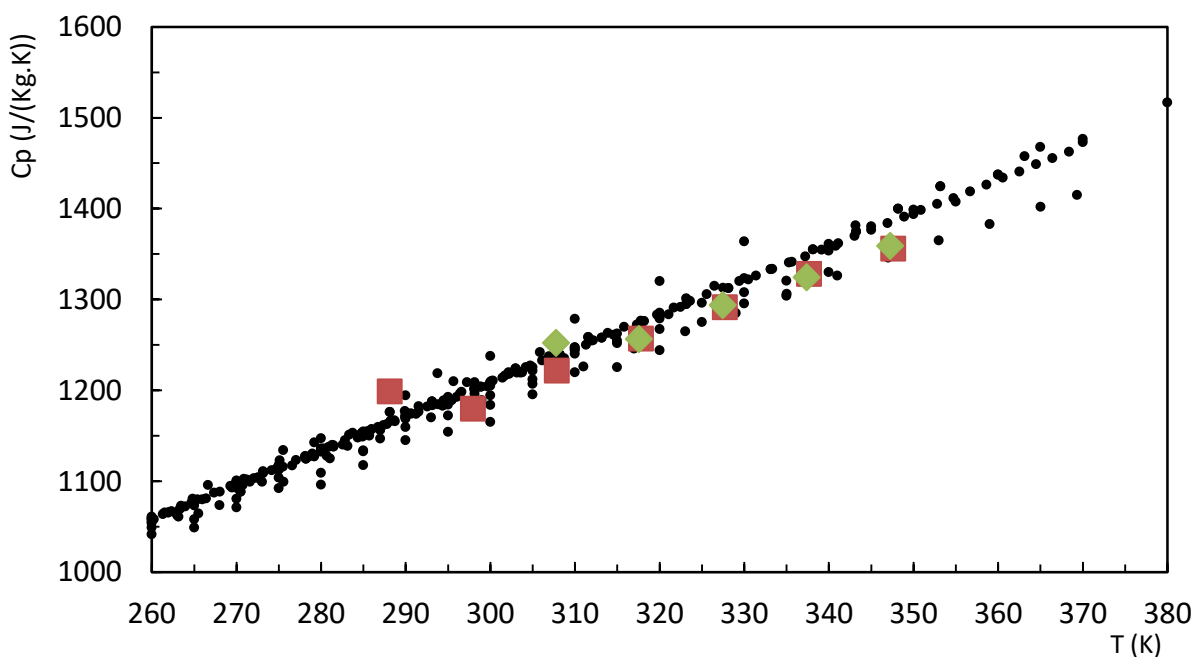


Figure 5 - Testing results of the heat capacities of Benzoic Acid with temperature. (●) Reference data; (■) Results in Calorimeter no. 1; (◆) Results in Calorimeter no. 2.

3. Results and Discussion

a) Phase Equilibria

i. Solubility of N₂

The solubility of N₂ in *1,4-butanediol* and *HDI*, measured at temperatures of 303.15 and 313.15 K and at pressures from nearly vacuum up to 8 bar are presented on the table 4 and plotted on figures 6 and 7.

Table 4 - Experimental solubilities of N₂ in 1,4-butanediol and HDI at 303.15 K and 313.15 K.

1,4-butanediol				HDI			
T = 303.15 K		T = 313.15 K		T = 303.15 K		T = 313.15 K	
P (bar)	x _{CO₂} (wt%)	P (bar)	x _{CO₂} (wt%)	P (bar)	x _{CO₂} (wt%)	P (bar)	x _{CO₂} (wt%)
0.001	0.000	0.003	0.000	0.000	0.000	0.004	0.000
0.568	0.004	0.515	0.004	0.500	0.006	0.451	0.005
1.629	0.013	1.012	0.007	1.017	0.013	1.062	0.013
2.208	0.017	2.001	0.015	1.999	0.025	2.053	0.025
3.105	0.025	3.013	0.023	3.074	0.039	3.027	0.037
4.086	0.033	4.016	0.030	4.044	0.052	4.005	0.049
5.089	0.042	5.062	0.038	5.039	0.066	5.061	0.062
6.091	0.050	6.034	0.047	6.067	0.080	6.029	0.075
7.101	0.059			7.056	0.093	7.038	0.088
8.097	0.068						

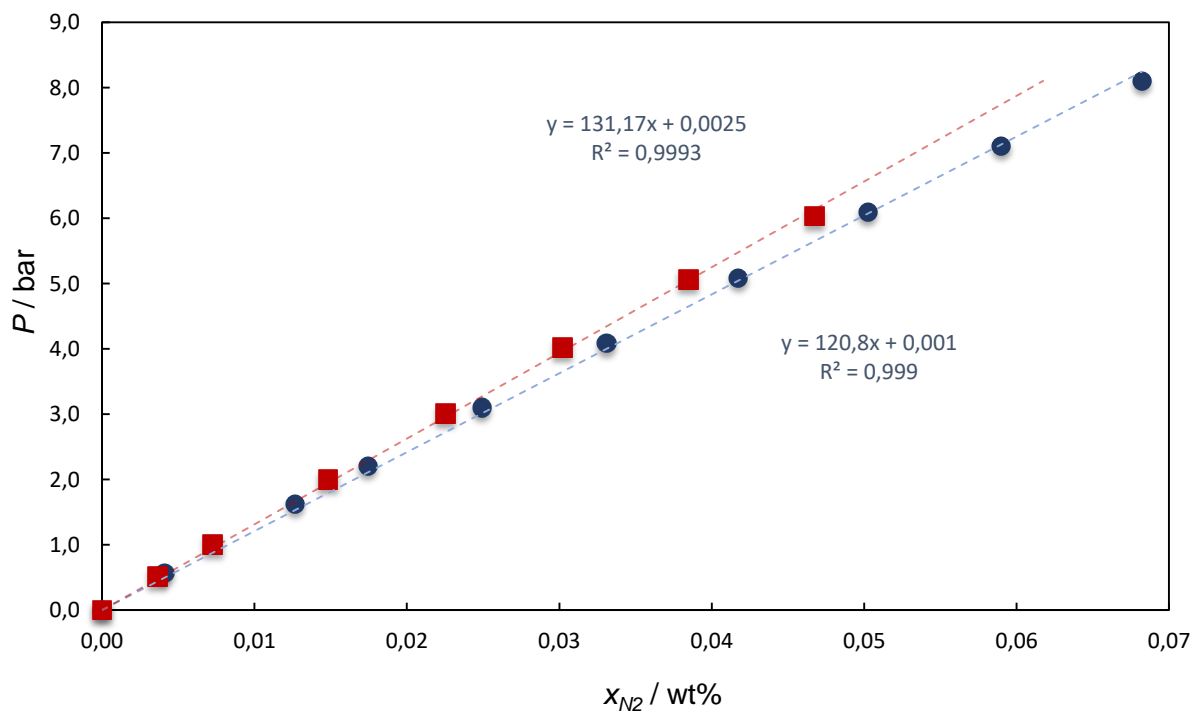


Figure 6 - Solubility of N₂ in 1,4-butanediol at 303.15 K (●) and 313.15 K (■).

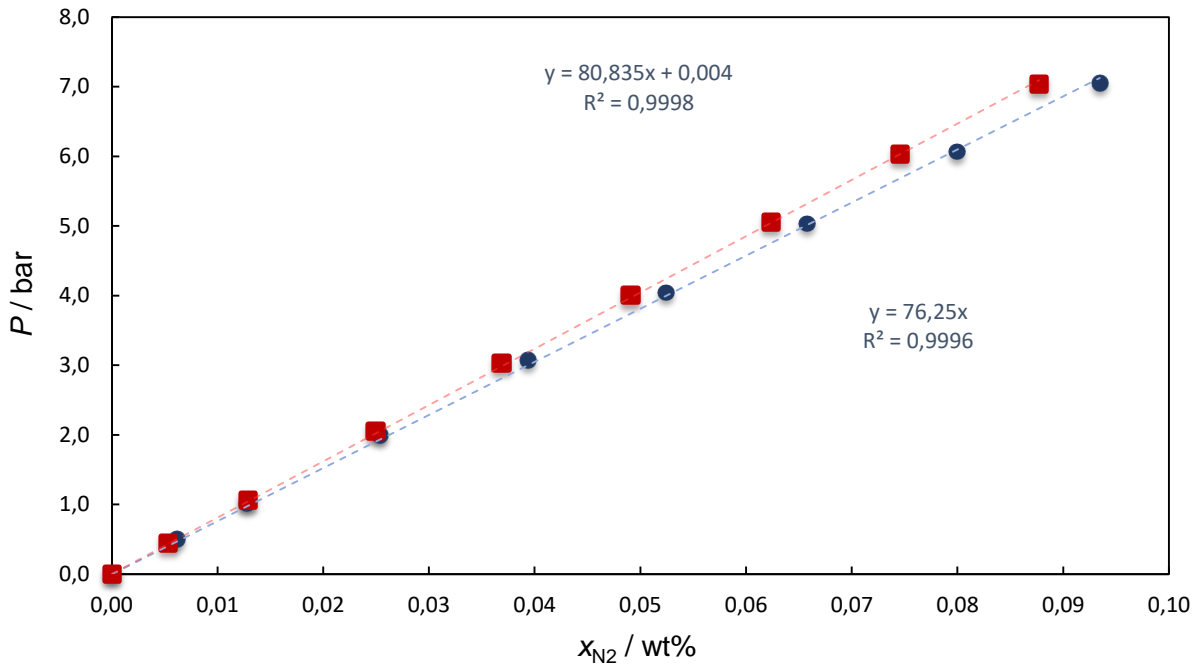


Figure 7 - Solubility of N₂ in HDI at 303.15 K (●) and 313.15K (■).

In both cases the plot show a linear increase of the solubility with pressure up to 7-8 bar, at which the concentrations are around 0.09 wt%. The solubility results of N₂ in 1,4-butanediol correspond to an Henry's Constant (Eq. 1) of $K_H \cong 3743$ bar and 4057 bar at temperatures of 303.15 K and 313.15 K, respectively. For HDI these values were calculated of $K_H \cong 1268$ bar and 1345 bar at temperatures of 303.15 K and 313.15 K, respectively.

$$K_H = P/x \quad (1)$$

For Henry's constant calculations it was used the molar fraction, even though mass fractions were used on the respective plots (Figures 6 and 7). It was also considered that the gas phases is composed only by Nitrogen which is not a big deviation from reality given the relatively low vapor pressure of both 1,4-butanediol and HDI..

ii. Solubility of CO₂

The solubilities of CO₂ in polymers PET-CO₂ type 5C and 10C were measured at temperatures of 353 K and 393 K and at pressures from nearly vacuum up to 80 bar. The results obtained are represent in table 5 and plotted in figures 8 and 9.

Table 5 - Experimental solubilities of CO₂ in PET-CO₂ Type 5c and 10c at 353.15K and 383.15K.

PET-CO ₂ Type 5C				PET-CO ₂ Type 10C			
T = 353.13 K		T = 393.15 K		T = 353.13 K		T = 393.15 K	
P (bar)	x _{CO₂} (wt%)	P (bar)	x _{CO₂} (wt%)	P (bar)	x _{CO₂} (wt%)	P (bar)	x _{CO₂} (wt%)
0.023	0.000	0.023	0.000	0.072	0.000	0.032	0.000
7.614	1.478	8.830	1.062	4.635	0.773	8.728	1.006
21.083	3.800	20.231	2.348	14.543	2.300	22.325	2.496
36.495	6.496	35.880	4.180	29.772	4.851	42.210	4.811
52.765	9.435	51.540	6.054	39.753	6.617	60.460	7.010
69.435	12.565	67.990	8.051			72.320	8.395

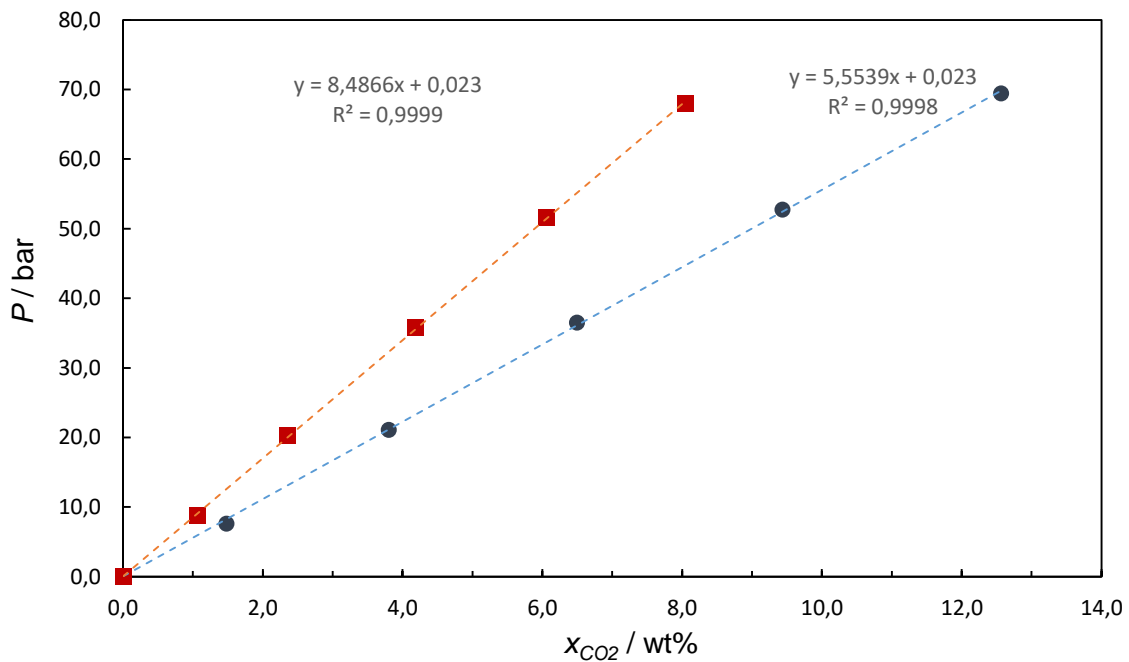


Figure 8- Experimental solubilities of CO₂ in PET-CO₂ Type 5c at 353.15K (●) and 383.15K (■).

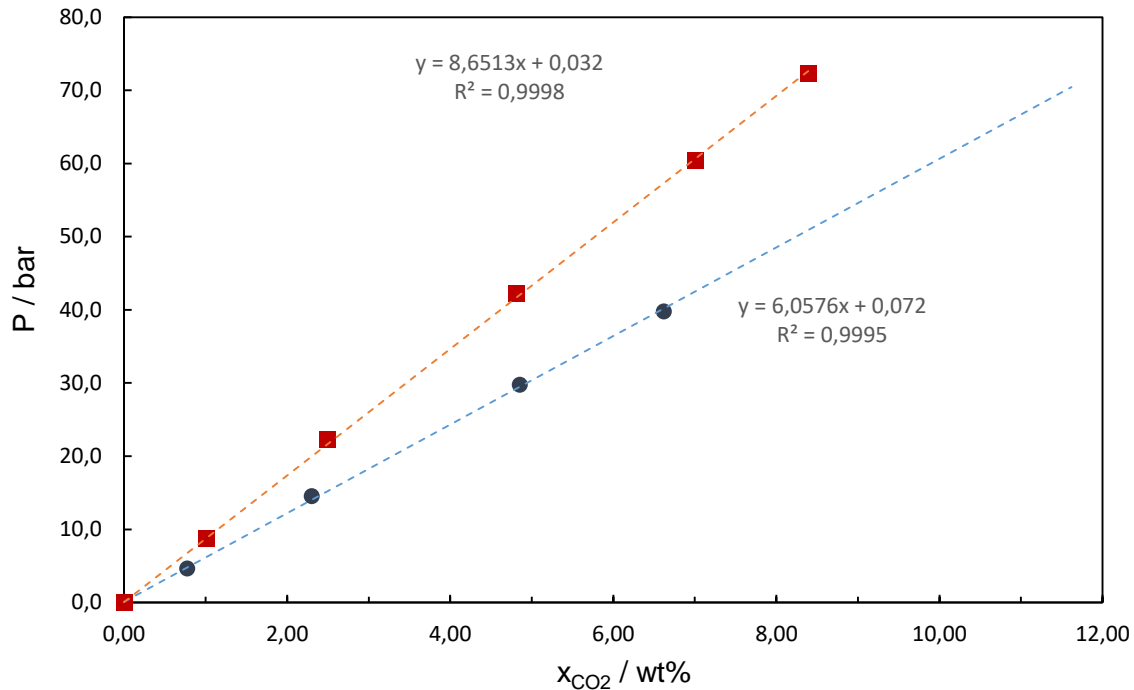


Figure 9 - Experimental solubilities of CO₂ in PET-CO₂ Type 10c at 353.15K (●) and 383.15K (■).

As it can be seen in plots 8 and 9 the solubilities of CO₂ can be considered as being linear with pressure and decrease with the increase of temperature, which is normally expected for the solubility of gas in condensed phases, and already showed in studies of similar systems by Fonseca (1) (2). Both polymers have similar structures, however PET-CO₂ Type 10C has a bigger molecular mass and a slight larger CO₂ content on its structure. It is verified that CO₂ has a larger solubility in polymer PET-CO₂ Type5c presenting amounts of gas dissolved less than 10% higher comparing to the PET-CO₂ Type 10c for the same pressure at 353 K and amounts less than 2% higher at 393 K. It is also verified that the solubility of CO₂ at 353 K is 34,6 % higher than at 393 K for the PET-CO₂ Type 5c Polymer and 30,0 % for PET-CO₂ Type 10c at same temperatures.

Lower solubility with high temperatures can be explained by the higher molecular agitation which leads to a weaker vapor-liquid interface and a higher molecular transit between phases.

In his first studies in 2012, Fonseca (1) measured the solubility of CO₂ in a polymer with similar structure, named PPP, obtaining values of around 8.7% at 383 K and 6.8% at 413 K at 70 bar. In 2015 Fonseca (2) measured the solubility of CO₂ in another similar polymer, named PET-CO₂ A, obtaining values of around 8.0% at 373 K and 75 bar and 6.5% at 393 K and 70 bar. In this work, the polymer PET-CO₂ Type 5c showed solubilities of 12.6% at 353 K and 8.1% at 393 K both at around 70bar which are results that follow a tendency observed by the 2 other studies, despite not having the exact same conditions.

b) Alcohols

i. Viscosity

The determination of viscosities was made in 9 different compositions for each mixture at temperatures of 283 K up to 313 K for the Butanol + PFB and and 353 K for the pair Hexanol + PFH (Appendix A1 and A2). Represented in Figure 9 is the growth of the viscosities with temperature of 4 compositions for each pair including pure compounds.

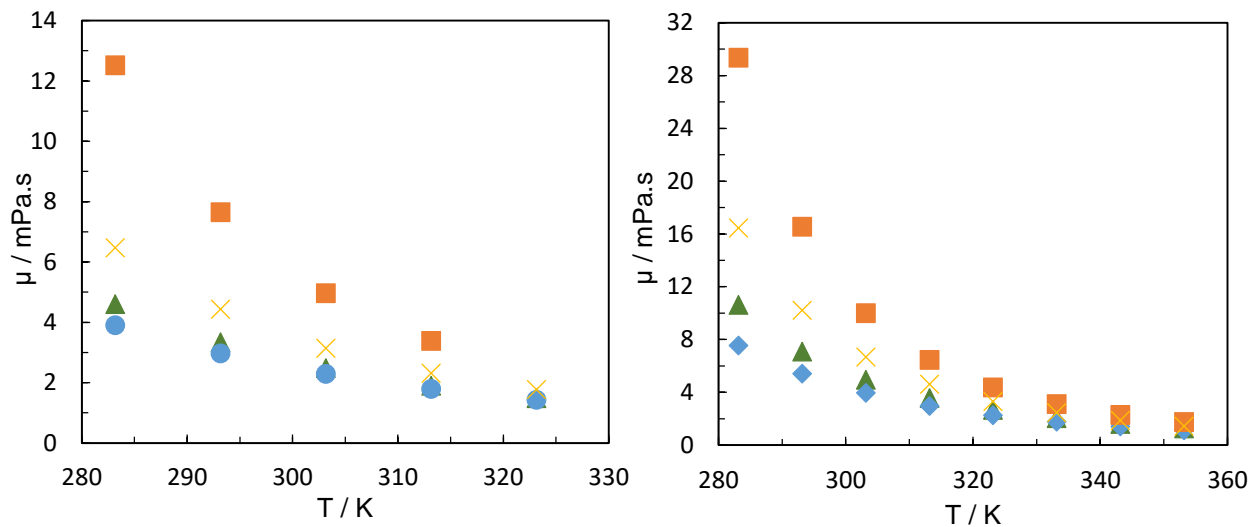


Figure 9 - Experimental values of the viscosity with Temperature for Butanol + PFB (A) and Hexanol + PFH pair (B). (●) $x(\text{PF})=0$; (▲) $x(\text{PF})=0,5$; (X) $x(\text{PF})=0,75$; (■) $x(\text{PF})=1$.

The measured viscosities for the pure hydrogenated compounds, *1-Butanol* and *1-Hexanol*, are compared with data from the literature in Figure 10. As can be seen, both experimental data fit on data from the literature, with general discrepancy lower than 1%.

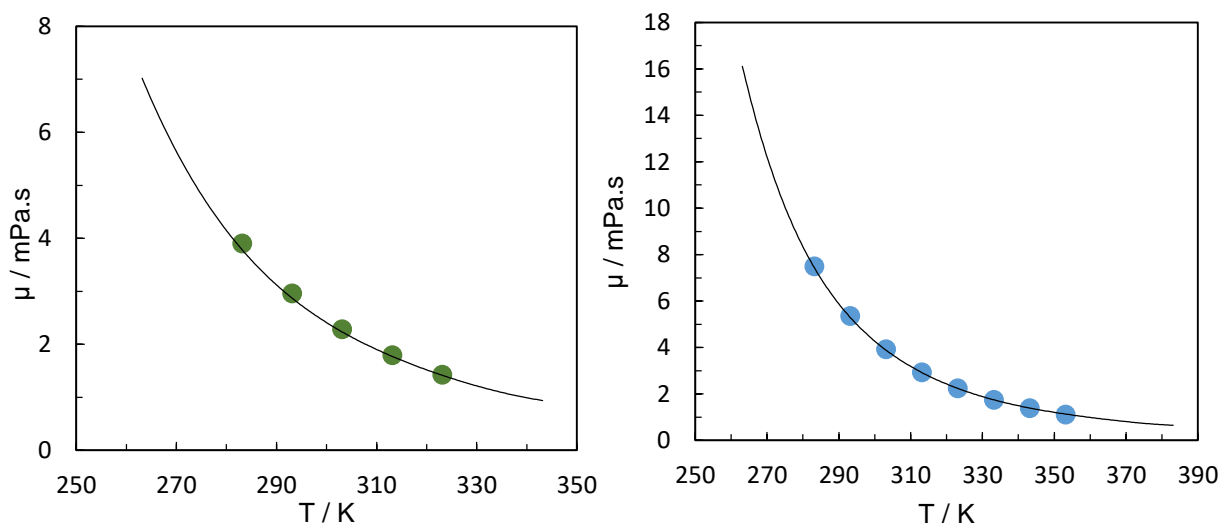


Figure 10 – Comparison of experimental viscosities (●) with values from literature* (represented by the the line) for pure compounds Butanol (A) and Hexanol (B) with temperature. *- DIPPR database from American Institute of Chemical Engineers.

The viscosities values of every composition for both pairs were grouped and it was determined the growth of the viscosity in whole composition range for a fixed temperature. As an example, it is plotted in Figure 11 the viscosity for both pairs at a temperature of 293.15 K with the comparison with the ideal behavior.

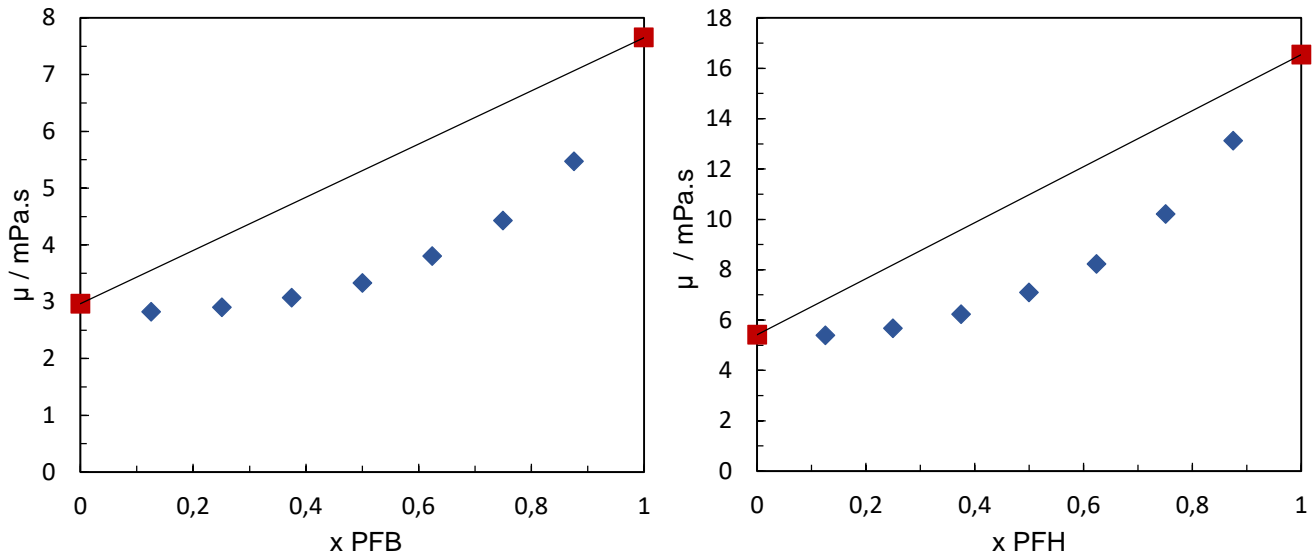


Figure 11 - Experimental viscosities as a function of composition of the fluorocompound at 293,15 K. A - But + PFB; B - Hex + PFH. The straight line represents the arithmetic mean of the pure compounds.

Through the difference between the measured viscosity and the ideal value (Eq.2) that is determined by a weighted average of the pure compound's viscosities (Eq.3) it was determined the Excess Viscosity (μ^E) for each composition for both pairs (figure 12).

$$\mu^E = \overline{\mu^{ideal}} - \mu \quad (2)$$

$$\overline{\mu} = \mu_1 x_1 + \mu_2 x_2 \quad (3)$$

The excess viscosity charts were built for both pair of alcohols with the results obtained for several temperatures over the entire composition range and are represented in the Figure 12. Excess viscosities with large negative deviations were already expected for both systems in this work (But+PFB and Hex+PFH) according to previous studies of similar compounds.

As it can be seen in Figure 12, both studied systems follow the expectations and show negative excess viscosities (μ^E). In the first case, butanol + PFB, the system shows excess viscosities up to -43,9% at 283K, -37,2% at 293K, -31,6% at 303K and -26,8% at 313K (Figure 12 A). In the second case, Hexanol + PFH, the system shows excess viscosities up to -42,4% at 283K, -35,3% at 293K, -29,1% at 303K, -24,2% at 313K, -19,8% at 323K, -16,4% at 333K, -13,2% at 343K and -11,2% at 353K (Figure 12 B).

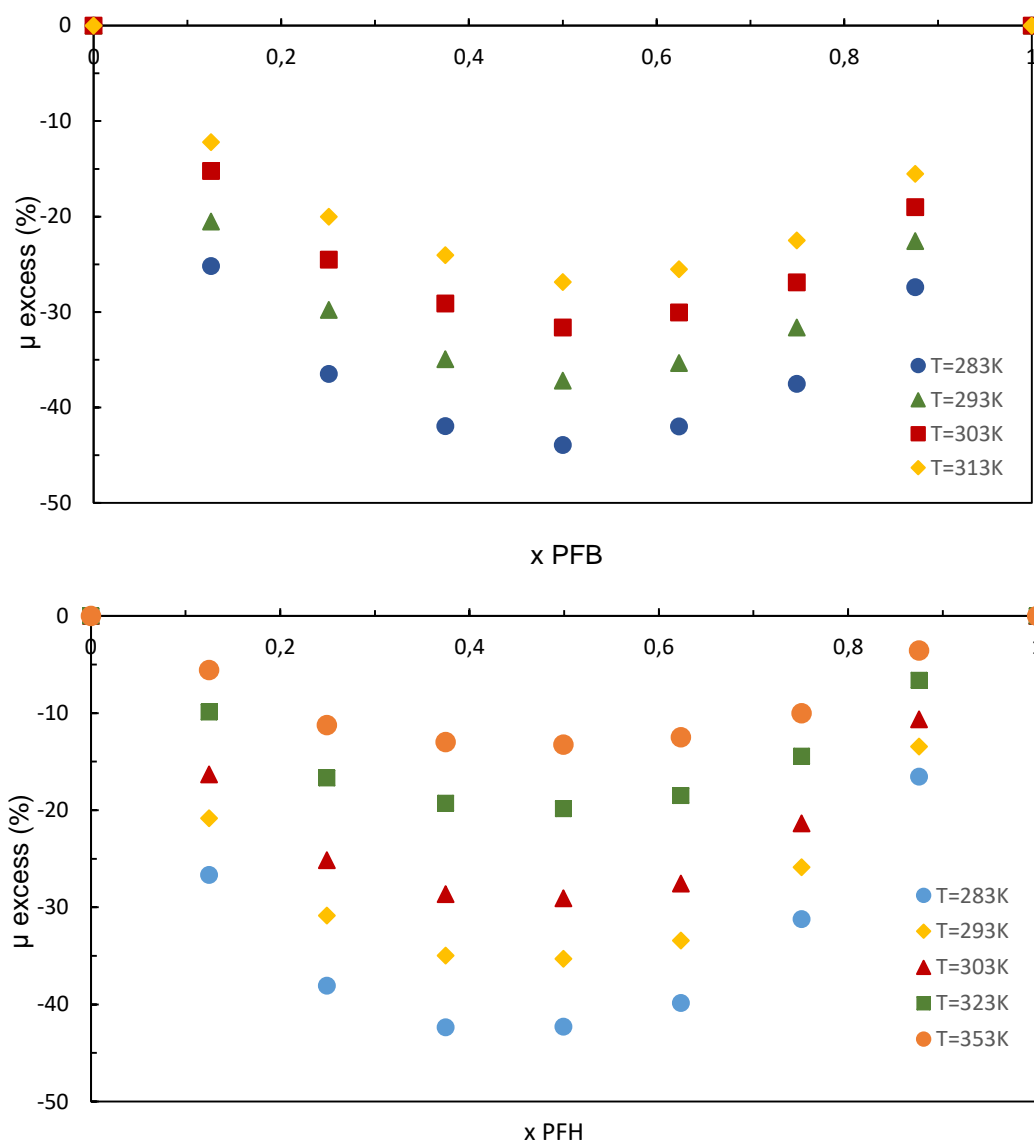


Figure 12 - Excess viscosities as a function of composition at several temperatures for pair Butanol + PFB (A) and Hexanol + PFH (B).

MORGADO et al (2013) (11) studied the excess viscosity of the binary mixture *Hexane + Perfluorohexane* obtaining negative deviations with values up to 17% below the arithmetic mean of pure compounds at a temperature of 298.15 K. These results are likely related to the dispersive forces of the hydrogenated and fluorinated chains in the mixture.

SHAN et al (1999) (22) measured viscosities of nine different binary mixtures of 1-alkanols. More in particular, Shan measured viscosities of the binary pair of *1-butanol* + *1-pentanol* and *1-butanol* + *1-nonanol* at 293.15 K and 298.15 K obtaining negative deviations up to -1,5% and -15%, respectively, when comparing to the arithmetic mean of the pure compounds. With alcohols, hydrogen bonds have to be taken in consideration, and Shan's results may indicate weaker bonds in the mixture when compared to the pure compounds.

In this work, both mixtures contain alcohols with hydrogenated and fluorinated chains, which relate in a different way to both studies referred above. The mixtures studied in this work, But+PFB and Hex+PFH showed negative deviations of the experimental viscosities at the temperature of 293.15 K up to -37% and -35%, respectively, when comparing to the arithmetic value of the pure compounds, which are larger than both studies referred above, which indicate stronger dispersive forces and weaker interactions between molecules.

ii. Heat Capacities

The heat capacity (C_p) of 9 known composition mixtures of each pair was measured from 293 K up to 333 K, in the case of butanol+PFB and from 303 K up to 333 K, for hexanol + PFH. In this limited temperature range, the heat capacity increases linearly with the temperature. The results of measured heat capacities for each composition of both mixtures in the valid temperature range are presented in Appendix B 1 and 2. The calculated linear correlations, that follow the equation 4, are represented on Table 6 with its respectively coefficient of determination (R^2).

$$C_p(J.K^{-1}mol^{-1}) = a \times T(K) + b \quad (4)$$

Table 6 - Linear regressions for experimental values of specific heat capacity with the temperature for the entire composition range, for both pairs of alcohols (Butanol + PFB and Hexanol + PFH).

Butanol + Perfluorobutanol				Hexanol + Perfluorohexanol			
x	$a (J.K^{-2}mol^{-1})$	$b(J.K^{-2}mol^{-1})$	R^2	x	$a (J.K^{-2}mol^{-1})$	$b(J.K^{-2}mol^{-1})$	R^2
0,000	0,838	-72,672	0,998	0,000	1,011	-60,545	0,9999
0,124	0,708	-21,325	0,996	0,126	0,949	-26,854	0,999
0,249	0,641	15,383	0,839	0,249	0,955	-7,466	0,996
0,373	0,627	30,473	0,995	0,374	0,833	50,285	0,999
0,501	0,592	60,149	0,991	0,495	0,778	89,317	0,994
0,626	0,669	49,981	0,998	0,622	0,688	139,009	0,992
0,750	0,744	41,973	0,998	0,751	0,595	191,994	0,965
0,875	0,889	14,376	0,989	0,875	0,432	265,543	0,992
1,000	0,960	12,091	0,997	1,000	0,426	280,125	0,999

With these correlations, it was built the chart that represents the growth of the heat capacity in whole composition range, for a predefined temperature. These charts were built for both pairs of alcohols at 313.15 K, as an example, and they are represented below on the Figure 13 as well as the ideal prevision, to compare deviations.

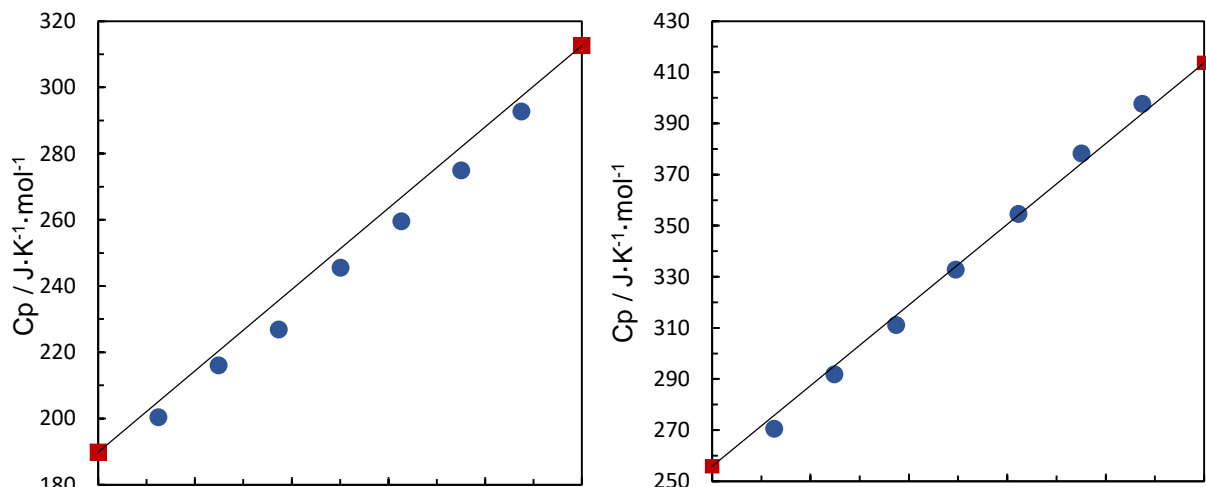


Figure 13 - Experimental values of Heat capacity as a function of the composition of the fluorocompound for pair Butanol + PFB (A) and Hexanol + PFH (B) at 313.15 K. The straight line represents the arithmetic mean of the pure compounds.

With these results, it is possible to represent the excess heat capacity (Cp^E) of every mixture. This derived property is also determined as the difference between the results obtained and the value as if the system was ideal (Eq.5), represented by the straight line on Figure 13, and calculated by a weighted average of the heat capacity of the pure compounds. (Eq.6)

$$Cp^E = \overline{Cp} - Cp \quad (5)$$

$$\overline{Cp} = x_1 Cp_1 + x_2 Cp_2 \quad (6)$$

The excess heat capacities obtained for both pairs of alcohols are represented on the charts on Figure 14, at temperatures of 298.15 K and 328.15 K for the mixture But+PFB and 308.15 K and 328.15 K for the mixture Hex+PFH.

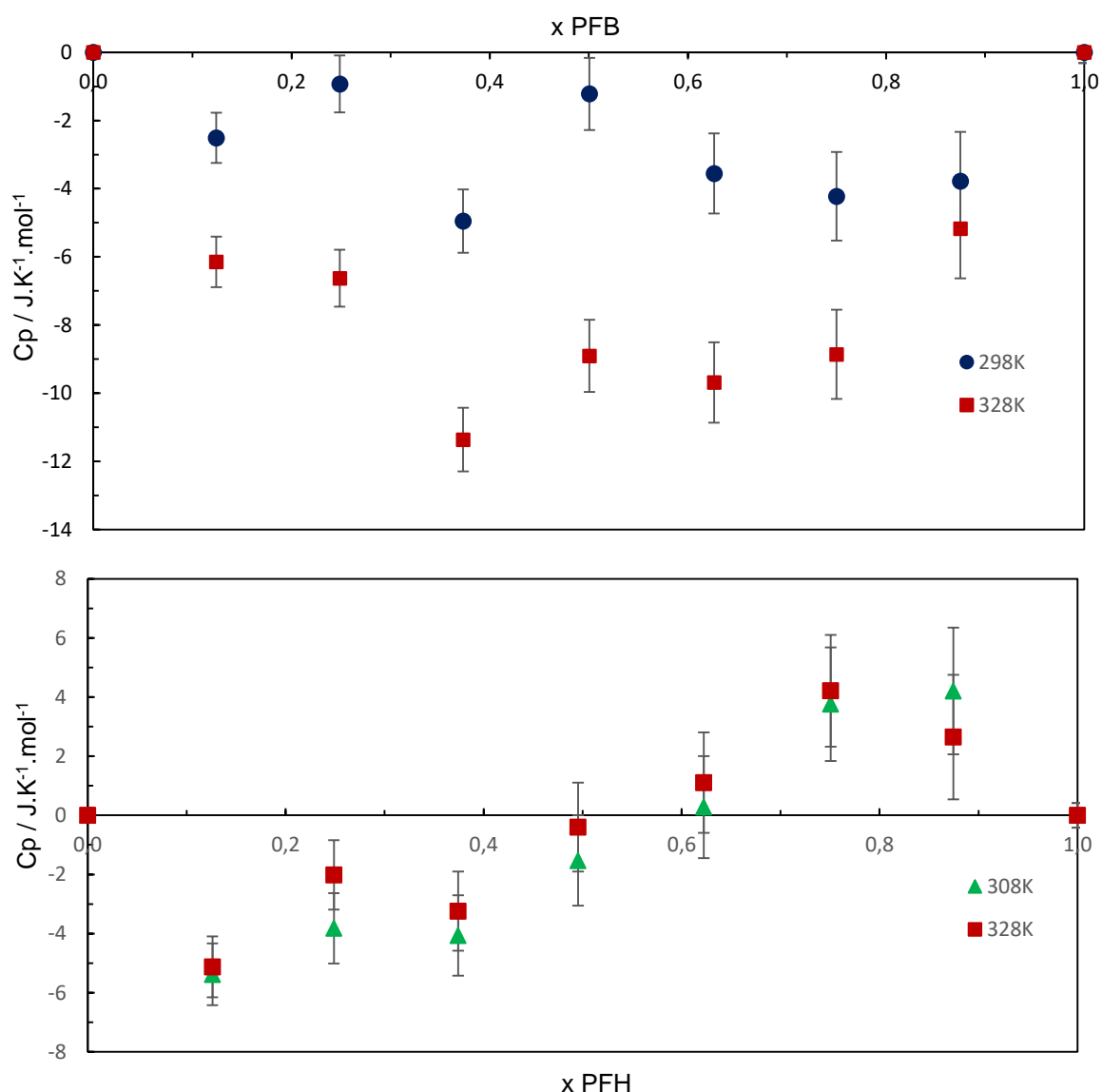


Figure 14 - Excess heat capacities as a function of composition of the fluorocompound at $T=298,15K$ (●) and $T=328,15K$ (■) for the pair Butanol + PFB (A) and at $T=308,15K$ (▲) and $T=328,15K$ (■) for the pair Hexanol + PFH (B).

As can be seen in Figure 13 A and B, the first pair of alcohols, Butanol + PFB, shows a negative deviation of the experimental values of CpE in its entire range. It was obtained values up to $-5.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 298.15 K and $-9.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 328.15 K which represent deviations of -2,3 % and -4,9 %, respectively. This behavior follows Yao's (19) studies that showed the CpE of mixture of primary hydrogenated alcohols is negative even though with relatively small values (e.g. $\sim -2 \%$ for the binary mixture 1-butanol + 1-decanol at 313.15 K), which induce weaker intermolecular forces, which in turn means that hydrogen bonds are stronger in the pure compounds than in the mixtures where hydrogenated and fluorinated chains have to pack together.

In the second case, Hexanol + PFH, show an S-shaped behavior of CpE's having a negative deviation to low concentrations of the perfluoroalkanol and a positive deviation to high concentrations, with values varying between $-5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $+4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for 308.15 K and 328.15 K which represent relative deviations of approximately between -2% and $+1 \%$. In both cases the inflexion points ($\text{CpE} = 0$) is around the equimolar fraction. These results induce that at low concentrations of PFH the intermolecular interactions are weaker than in pure compounds hypothetically caused by the weakening of the hydrogen bonds when in presence of both hydrogenated and fluorinated chains in solution. However, at higher concentrations of PFH, when the 'chain conformation' is harder due to higher presence of fluorinated tails, the deviation of CpE become positive, which contradicts everything else that has been concluded about mixtures of hydrogenated and fluorinated compounds so far. Despite not having an explanation for the phenomena, these results go accordingly what Lepori (10) determined when studying the excess enthalpy (HE) of the binary mixture hexane + perfluorohexane, which also could not explain the unexpected results.

4. Conclusions

In the first part of this work it was measured the solubilities of nitrogen in 1,4-butanediol and in hexamethyl diisocyanate, which are 2 important monomers being used in the production of an innovative polymer., The solubilities of Nitrogen were measured at temperatures of 303.15 K and 313.15 K at pressures from nearly vacuum up to 8 bar for both monomers. With the experimental values it was calculated the Henry's constant for both compounds. As it was expected the solubility of Nitrogen decreases with temperature.

For the optimization of production process of CardyonTM, an innovative polymer using carbon dioxide (CO₂) as raw material, the solubility of CO₂ in 2 different polycarbonates (PET-CO₂ Type 05c and type10c) was measured at temperatures of 353.15 K and 383.15 K at equilibrium pressures from nearly vacuum up to 70 bar. The results showed that solubility of carbon dioxide is higher in the Type 5c polymer, presenting amounts of gas dissolved around 10% higher at 353 K and around 2% higher at 393 K, compared to the Type 10c polymer. The results also showed, as it was expected, that the solubility of CO₂ decreases with the temperature, which can be explained by the higher molecular agitation caused by the temperature, which leads to a weaker vapor-liquid interface and a higher molecular transit between phases.

In the second part of this work, it was studied two binary mixtures of alcohols, 1-butanol + 1H, 1H-Heptafluorobutanol and 1-Hexanol + 1H, 1H-Undecafluorohexanol in its entire composition range. These mixtures have a complex behavior when compared to equivalents mixtures, of hydrogenated alcohols or even with alkane + perfluoroalkane mixtures. The fluorinated chains have a very particular behavior and it combined with different states of hydrogen bonding can be challenging to understand.

It was determined the viscosities at temperatures from 293 K up to 323 K and 353 K, with 10 K steps, for the But+PFB and Hex+PFH mixture, respectively. The results of the hydrogenated pure compounds were confirmed with some results from DIPPR database with high concordance. With the results it was calculated the excess viscosity, which was determined as the difference between the experimental results and the arithmetic mean of the pure compounds. The results showed a negative parabolic behavior of excess viscosities with the composition, with decreasing values with temperature. These results induce that the dispersive forces between hydrogenated and fluorinated chains are stronger than the cohesive forces, hydrogen bonding, which was already expected by previous work in the same subject, and by viscosity studies of binary mixtures of 1-alkanols and alkane - perfluoroalkane (16) (11) (22).

It was also determined the heat capacities of both mixtures in its entire composition range, at temperatures from 293 K up to 323 K and 353 K, for the But+PFB and Hex+PFH mixture, respectively. With these results it was calculated the excess heat capacity, which was determined as the difference between the experimental results and the arithmetic mean of the pure compounds. For the binary mixture But+PFB it was obtained a negative parabolic deviation with relatively small values which follows a similar enthalpy study of binary mixtures of 1-alkanols (19), which, once again, induces weaker intermolecular interactions between hydrogenated and fluorinated compounds. In the second case, the binary mixture Hex+PFH the excess heat capacities results showed a S-shaped behavior, with negative deviations to low concentrations of the fluorinated alcohol and becoming positive to compositions higher than approximately the equimolar fraction. These results, to low concentrations of fluorinated tails, follow what have been concluded so far, since negative deviations induce weaker interaction between molecules, caused by the dispersive forces of the apolar chains, however, to higher concentrations of PFH, the deviations become positive which follows the results of the excess heat capacity for the binary mixture alkane + perfluoroalkane, obtained by Lepori (10) even though its contradicts everything that has been studied with binary mixtures of hydrogenated and fluorinated compounds, and cannot be explained.

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6. Appendixes

A 1 – Viscosities obtained and respective calculated excess viscosities for the 9 compositions of the mixtures But+ PFB at several temperatures.

But + PFB	x = 0		x = 0,1252		x = 0,2508		x = 0,3748		x = 0,5000	
	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)
283,15	3,9038	0,00	3,7281	25,16	3,8514	36,48	4,1401	41,94	4,6040	43,91
293,16	2,9628	0,00	2,8220	20,45	2,9068	29,76	3,0712	34,93	3,3338	37,19
303,15	2,2876	0,00	2,2235	15,26	2,2335	24,51	2,3326	29,11	2,4792	31,61
313,15	1,7943	0,00	1,7494	12,20	1,7527	20,01	1,8134	24,05	1,8916	26,85

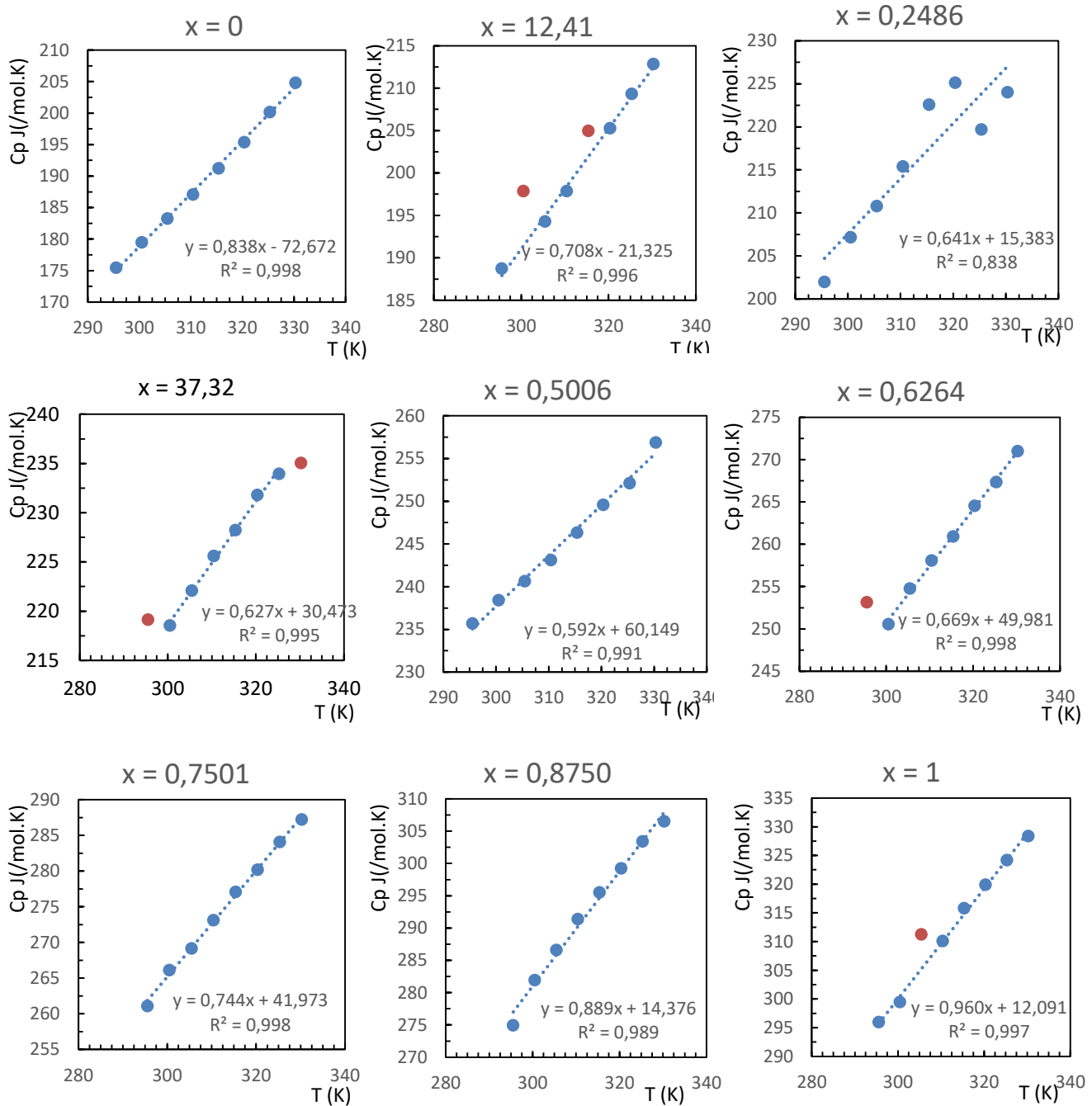
But + PFB	x = 0,6239		x = 0,7497		x = 0,8758		x = 1,0000	
	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)
283,15	5,3821	41,97	6,4715	37,52	8,3095	27,39	12,5130	0,00
293,16	3,8069	35,34	4,4292	31,62	5,4726	22,57	7,6502	0,00
303,15	2,7678	30,05	3,1388	26,89	3,7508	19,00	4,9629	0,00
313,15	2,0718	25,52	2,3102	22,50	2,6871	15,51	3,3768	0,00

A 2 – Viscosities obtained and respective calculated excess viscosities for the 9 compositions of the mixtures Hex + PFH at several temperatures.

Hex + PFH	x = 0		x = 0,1250		x = 0,2495		x = 0,3749		x = 0,4993	
	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)
283,15	7,5411	0,00	7,5316	26,65	8,0424	38,06	9,0605	42,36	10,6410	42,27
293,15	5,4145	0,00	5,3893	20,82	5,6659	30,84	6,2357	34,97	7,1010	35,29
303,15	3,9647	0,00	3,9502	16,30	4,0945	25,15	4,4446	28,63	4,9493	29,07
313,15	2,9710	0,00	2,9698	12,82	3,0514	20,54	3,2684	23,59	3,5696	24,22
323,15	2,2740	0,00	2,2865	9,88	2,3325	16,68	2,4728	19,28	2,6662	19,82
333,15	1,7726	0,00	1,7953	7,45	1,8204	13,57	1,9175	15,68	2,0412	16,36
343,15	1,4077	0,00	1,4347	5,56	1,4472	11,22	1,5158	12,98	1,6076	13,23
353,15	1,1352	0,00	1,1647	3,88	1,1799	8,38	1,2305	9,83	1,2800	11,16

Hex + PFH	x = 0,6235		x = 0,7510		x = 0,8751		x = 1,0000	
	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)	μ (mPa.s)	μ^E (%)
283,15	12,7180	39,84	16,4537	31,22	22,222	16,55	29,3545	0,00
293,15	8,2293	33,40	10,2100	25,88	13,1223	13,43	16,5475	0,00
303,15	5,5994	27,54	6,6824	21,36	8,2614	10,65	10,0001	0,00
313,15	3,9744	22,73	4,6049	17,59	5,5046	8,56	6,4551	0,00
323,15	2,9239	18,49	3,2987	14,44	3,8443	6,62	4,3799	0,00
333,15	2,2152	15,02	2,4478	11,86	2,7974	4,95	3,1102	0,00
343,15	1,7183	12,48	1,8691	10,01	2,1102	3,54	2,2989	0,00
353,15	1,3609	10,28	1,4486	9,16	1,6306	2,40	1,7471	0,00

B 1 – Heat capacities values with temperature obtained for the 9 compositions of the mixture But + PFB.



B 2 – Heat capacities values with temperature obtained for the 9 compositions of the mixture Hex + PFH.

