

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

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## 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<sub>2</sub>) 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<sub>2</sub>) as raw material, the solubility of CO<sub>2</sub> 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.

## 1.Introduction

Carbon dioxide (CO<sub>2</sub>) currently is and has been for 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). 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 direct chemical application of CO<sub>2</sub> 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 CO<sub>2</sub> 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).

The use of CO<sub>2</sub> as a raw material in the production of polymers had being considered for a long time, but the reaction of CO<sub>2</sub> revealed to be extremely unfavorable from the energetic point of view.

These thermodynamic limitations were overcome with the use of high energetic monomers like

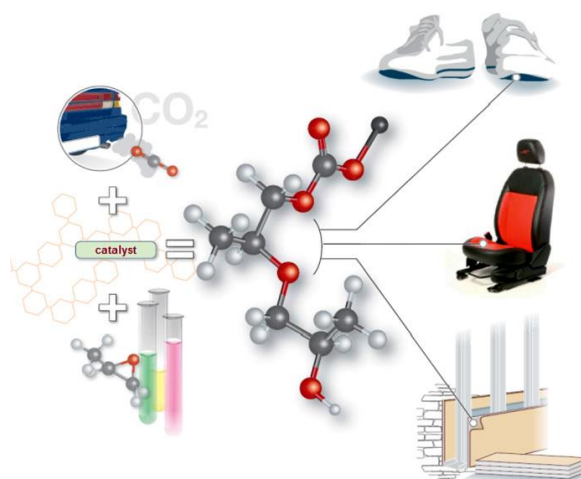


Figure 1 - Illustration of the use of CO<sub>2</sub> as a raw material in the production of polyurethanes used for diverse industries. Courtesy of Bayer AG (1).

epoxides in combination with the development of appropriate catalysts (Figure 2).

Using such tailored polymers in the production of polyurethanes is demonstrated as a great example for a novel CO<sub>2</sub> utilization with huge industrial potential and nowadays a pilot plant is already built and successfully producing high quality polymers with an incorporation of CO<sub>2</sub> above 20% wt (4).

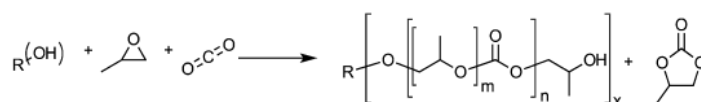


Figure 2 - Representation of the general chemical reaction for the production of Polyether Polycarbonate Polyols.

## 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).

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 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)

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

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)

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. In this work will be studied the excess viscosity and excess heat capacities of 2 mixtures of alcohols.

This work includes the study of mixtures containing fluorotelomer alcohols which are highly fluorinated molecules with a functional head, in this case an alcoholic group -OH with a general formula  $CF_3(CF_2)_n(CH_2)_mOH$  (in this work  $n = 2, 3$  &  $m = 1$ ). 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).

### 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 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).

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. This results in an organized microheterogeneous structure that reflect 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).

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. 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  $F_6 + H_n$  and  $H_6 + F_n$  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.

#### i. Solubilities of $N_2$

The solubility of Nitrogen ( $N_2$ ), bought from Linde with 0.99999 purity, was measured in 1,4-butanediol, bought from Merck with a purity higher than 0.99, and HDI, produced by a pilot plant in Covestro AG, from at pressures up to 8 bar and at temperatures of 303 and 313 K. In these experiments a full stainless-steel equilibrium cell was used, with an operating pressure range up to 40 bar, immersed in a thermal bad 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  $\pm 0,001bar$  and an accuracy of 0.05 % FS. The calculation of the solubility is made through an iterative process demonstrated in Figure 3. The precise amount of Nitrogen in the cell was determined using an equation of state by Span and Wagner (20).

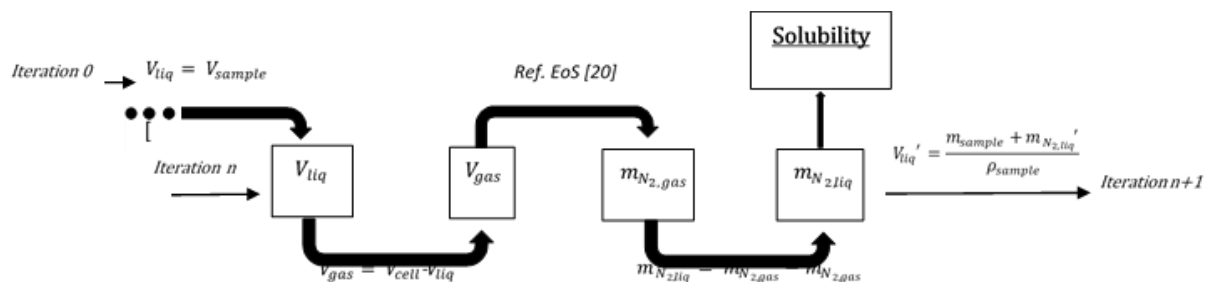


Figure 3 - Systematization of the iterative process used to calculate solubilities.

The solubility of CO<sub>2</sub>, bought from *Linde* with a purity of 0.99995, was measured in two different types of PET-CO<sub>2</sub> 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 are represented in the table 1. It was used a cylindrical cell with a 360° sapphire glass window immersed in a thermal bath. The chosen thermal fluid was *polyethylene glycol*. The exact amount of CO<sub>2</sub> was determined by the equation proposed by Span and Wagner (21). 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 CO<sub>2</sub> dissolved.

### a) 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), all bought from *Linde* with a purity higher than 0.99 in exception of PFH that was bought from ABCR with a purity of >0.98. The mixtures were prepared through mass weighing with precision of ±0.01g. Alcohols are hygroscopic, and so they were previously dried with molecular sieves and every sample were prepared in a glove box, under Nitrogen atmosphere.

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 heat capacities was measured at temperatures from 293 and 303 K up to 323 K for the mixture But+PFB and up to 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 +/- 1%. The Cp were measured using a step method, using temperatures 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 Cp 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 4).

Compound	Molecular Structure	Name	Hidroxyll Number	Mn [g/mol]	CO <sub>2</sub> [wt%]
Polyether Polycarbonate Polyols (PET-CO <sub>2</sub> )		Type 5C	56.4	1989	18
		Type 10C	56.2	2795	20

Table 1 - Identification, structure and some properties of both PET-CO<sub>2</sub> polymers studied.

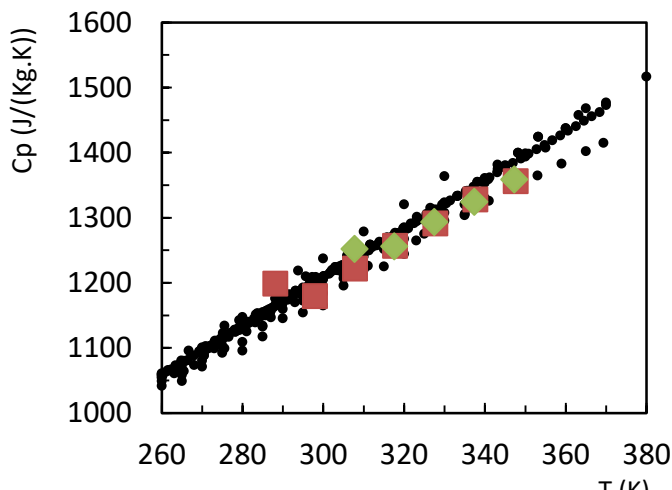


Figure 4 - Testing results of the heat capacities of Benzoic Acid with temperature. (●) Reference data; (■) Results in Calorimeter no.1; (◆) Results in Calorimeter no.2.

### 3. Results and Discussion

#### a) Phase Equilibria

##### i. Solubility of N<sub>2</sub>

The solubility of N<sub>2</sub> 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 2 and plotted on figures 5.

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 N<sub>2</sub> 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.

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

Table 2 - Experimental solubilities of N<sub>2</sub> 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 <sub>CO<sub>2</sub></sub> (wt%)	P (bar)	x <sub>CO<sub>2</sub></sub> (wt%)	P (bar)	x <sub>CO<sub>2</sub></sub> (wt%)	P (bar)	x <sub>CO<sub>2</sub></sub> (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						

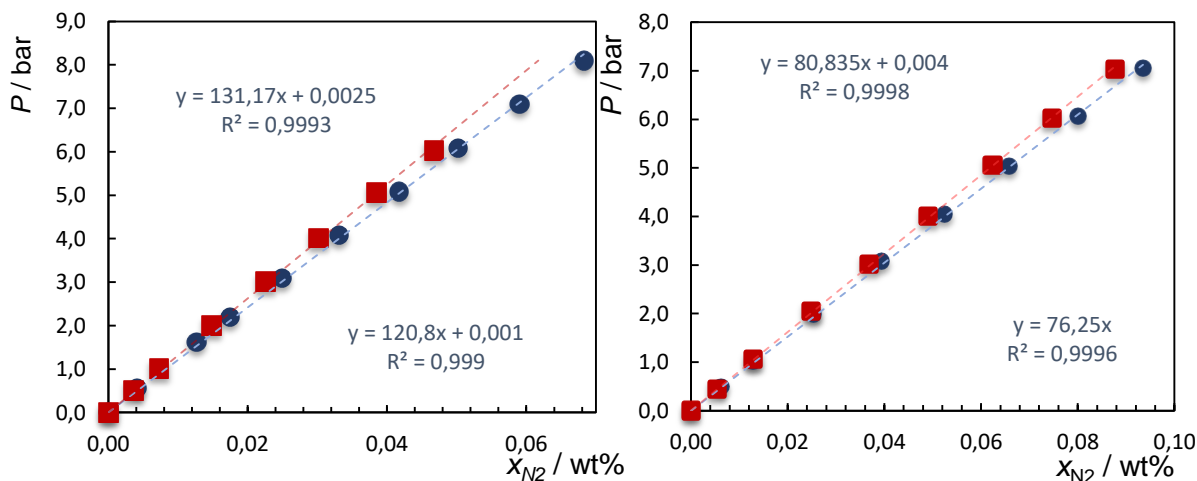


Figure 5 - Solubility of N<sub>2</sub> in 1,4-butanediol (A) and in HDI (B) at 303.15 K (●) and 313.15 K (■).

For Henry's constant calculations it was used the molar fraction, even though mass fractions were used on the respective plots (Figures 5). 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 CO<sub>2</sub>

The solubilities of CO<sub>2</sub> in polymers PET-CO<sub>2</sub> 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 3 and plotted in figures 6.

As it can be seen in plots 6 the solubilities of CO<sub>2</sub> 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-CO<sub>2</sub> Type 10C has a bigger molecular mass and a slight larger CO<sub>2</sub> content on its structure.

It is verified that CO<sub>2</sub> has a larger solubility in polymer PET-CO<sub>2</sub> Type5c presenting amounts of gas dissolved less than 10% higher comparing to the PET-CO<sub>2</sub> 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 CO<sub>2</sub> at 353 K is 34,6 % higher than at 393 K for the PET-CO<sub>2</sub> Type 5c Polymer and 30,0 % for PET-CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> in another similar polymer, named PET-CO<sub>2</sub> 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-CO<sub>2</sub> 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.

Table 3- Experimental solubilities of CO<sub>2</sub> in PET-CO<sub>2</sub> Type 5c and 10c at 353.15K and 383.15K

PET-CO <sub>2</sub> Type 5C				PET-CO <sub>2</sub> Type 10C			
T = 353.13 K		T = 393.15 K		T = 353.13 K		T = 393.15 K	
P (bar)	x <sub>CO<sub>2</sub></sub> (wt%)	P (bar)	x <sub>CO<sub>2</sub></sub> (wt%)	P (bar)	x <sub>CO<sub>2</sub></sub> (wt%)	P (bar)	x <sub>CO<sub>2</sub></sub> (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

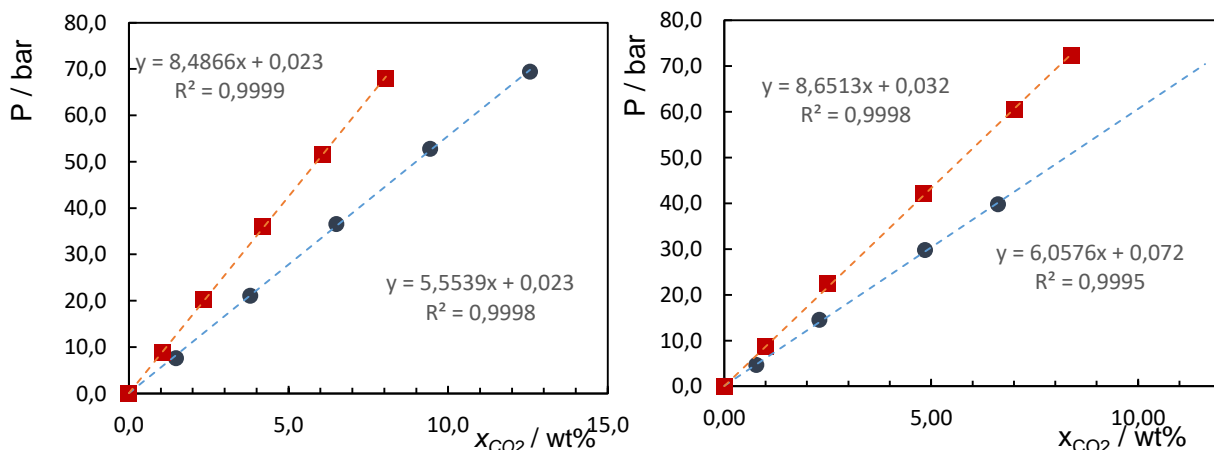


Figure 6 - Experimental solubilities of CO<sub>2</sub> in PET-CO<sub>2</sub> Type 5c at 353.15K (●) and 383.15K (■).

## 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. Represented in Figure 7 is the growth of the viscosities with temperature of 4 compositions for each pair including pure compounds.

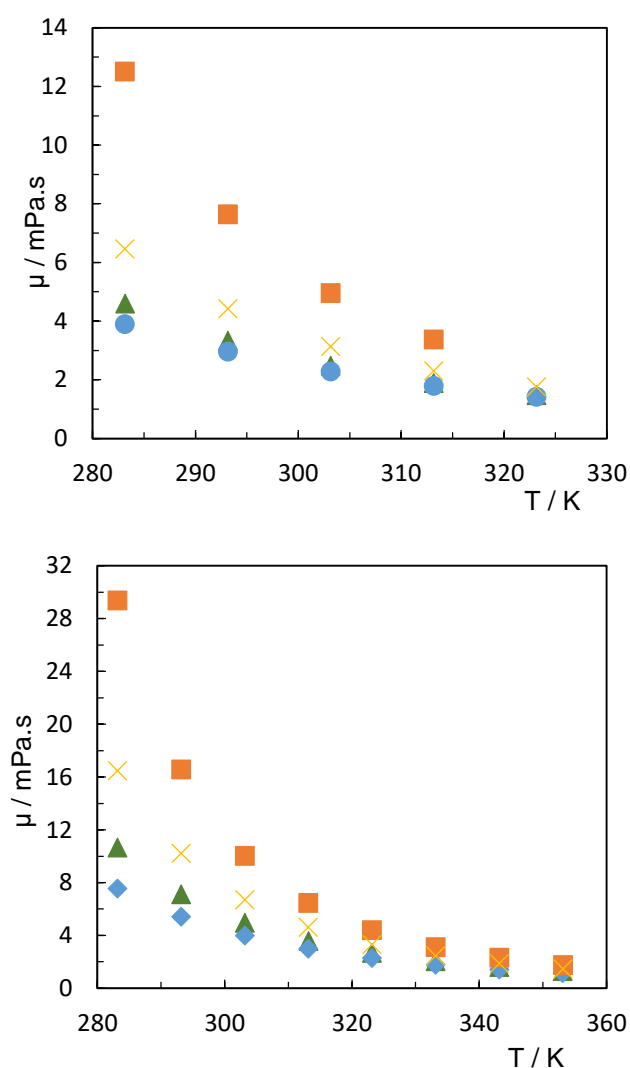


Figure 7 - Experimental values of the viscosity with Temperature for Butanol + PFB (A) and Hexanol + PFH pair (B). (●)  $x(PF)=0$ ; (▲)  $x(PF)=0,5$ ; (X)  $x(PF)=0,75$ ; (■)  $x(PF)=1$ .

The measured viscosities for the pure hydrogenated compounds, *1-Butanol* and *1-Hexanol*, are compared with data from the literature in Figure 8. As can be seen, both experimental data fit on data from the literature, with general discrepancy lower than 1%.

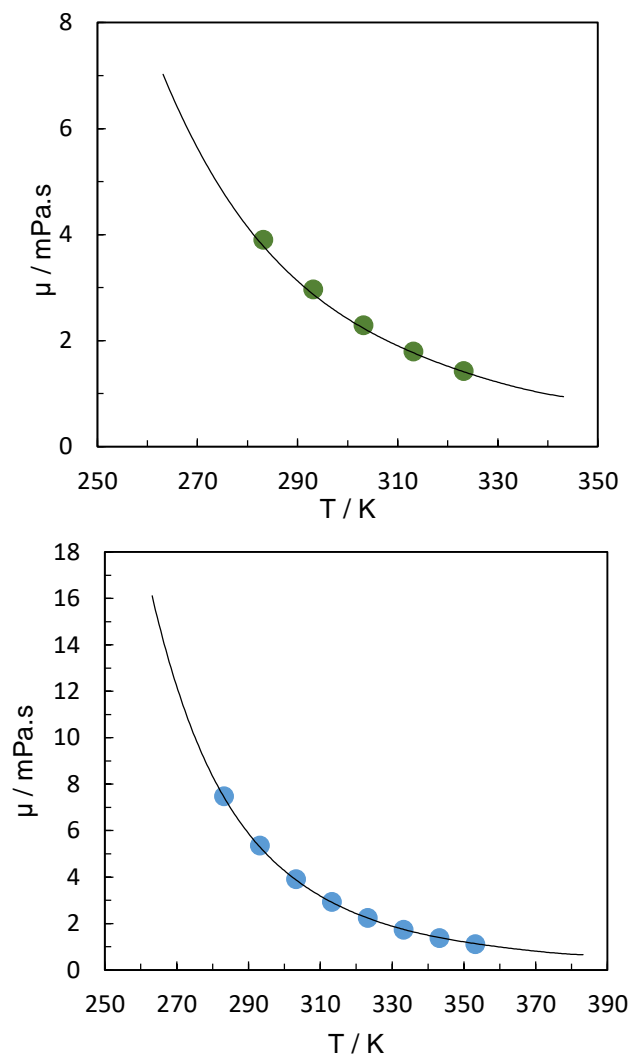


Figure 8 – Comparison of experimental viscosities (●) with values from literature\* (represented by the the line) for pure compounds Butanol (A) and Hexanol (B) with temperature. \*- DIPPR database from American Institute of Chemical Engineers. A – But + PFB; B- Hex+ PFH

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 9 the viscosity for both pairs at a temperature of 293.15 K with the comparison with the ideal behavior.

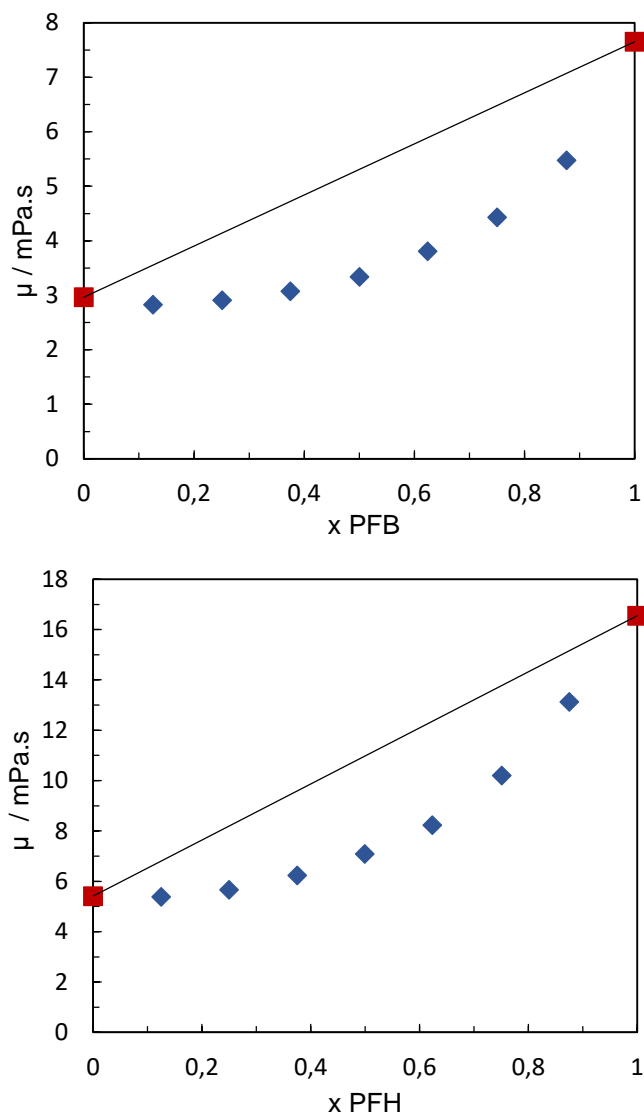


Figure 9 - Experimental viscosities as a function of composition of the fluorocompound at 293,15 K. A - But + PFB; B - Hex + PFH. The straight line represents the arithmetic mean of the pure compounds.

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 ( $\mu^E$ ) for each composition for both pairs (figure 10).

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

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

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 10. 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.

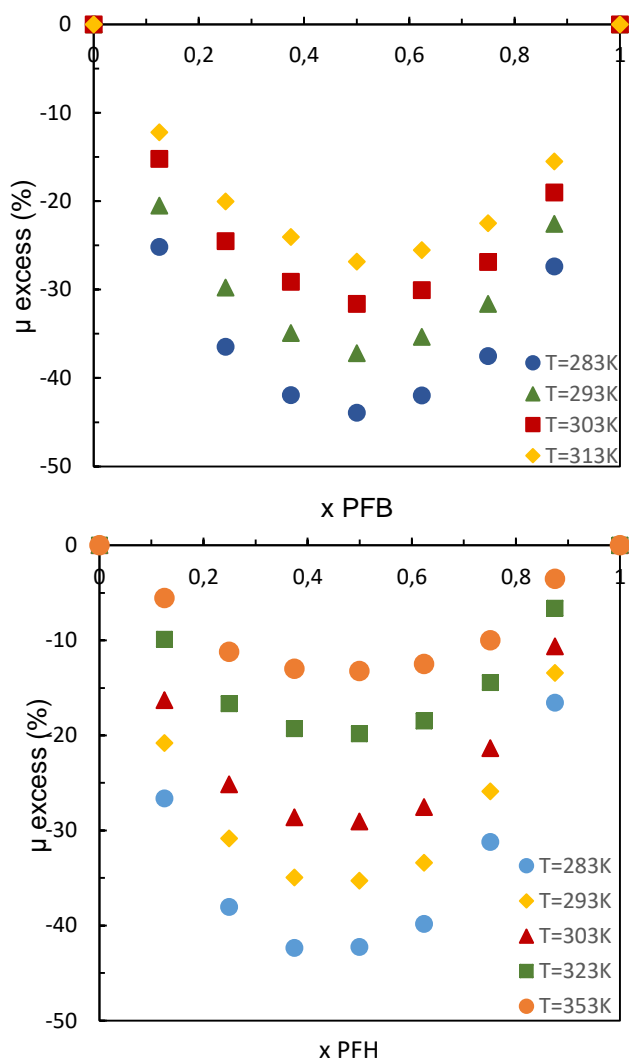


Figure 10 - Excess viscosities as a function of composition at several temperatures for pair Butanol + PFB (A) and Hexanol + PFH (B).



As it can be seen in Figure 10, both studied systems follow the expectations and show negative excess viscosities ( $\mu^E$ ). 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).

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 and it was calculated correlations for every composition that follow the equation 4. The correlations are represented on Table 4 with its respectively coefficient of determination ( $R^2$ ).

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

Table 4 - 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*).

<b>Butanol + Perfluorobutanol</b>				<b>Hexanol + Perfluorohexanol</b>			
$x$	$a (J.K^{-2}mol^{-1})$	$b(J.K^{-2}mol^{-1})$	$R^2$	$x$	$a (J.K^{-2}mol^{-1})$	$b(J.K^{-2}mol^{-1})$	$R^2$
<b>0,000</b>	0,838	-72,672	0,998	<b>0,000</b>	1,011	-60,545	0,9999
<b>0,124</b>	0,708	-21,325	0,996	<b>0,126</b>	0,949	-26,854	0,999
<b>0,249</b>	0,641	15,383	0,839	<b>0,249</b>	0,955	-7,466	0,996
<b>0,373</b>	0,627	30,473	0,995	<b>0,374</b>	0,833	50,285	0,999
<b>0,501</b>	0,592	60,149	0,991	<b>0,495</b>	0,778	89,317	0,994
<b>0,626</b>	0,669	49,981	0,998	<b>0,622</b>	0,688	139,009	0,992
<b>0,750</b>	0,744	41,973	0,998	<b>0,751</b>	0,595	191,994	0,965
<b>0,875</b>	0,889	14,376	0,989	<b>0,875</b>	0,432	265,543	0,992
<b>1,000</b>	0,960	12,091	0,997	<b>1,000</b>	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 11 as well as the ideal prevision, to compare deviations.

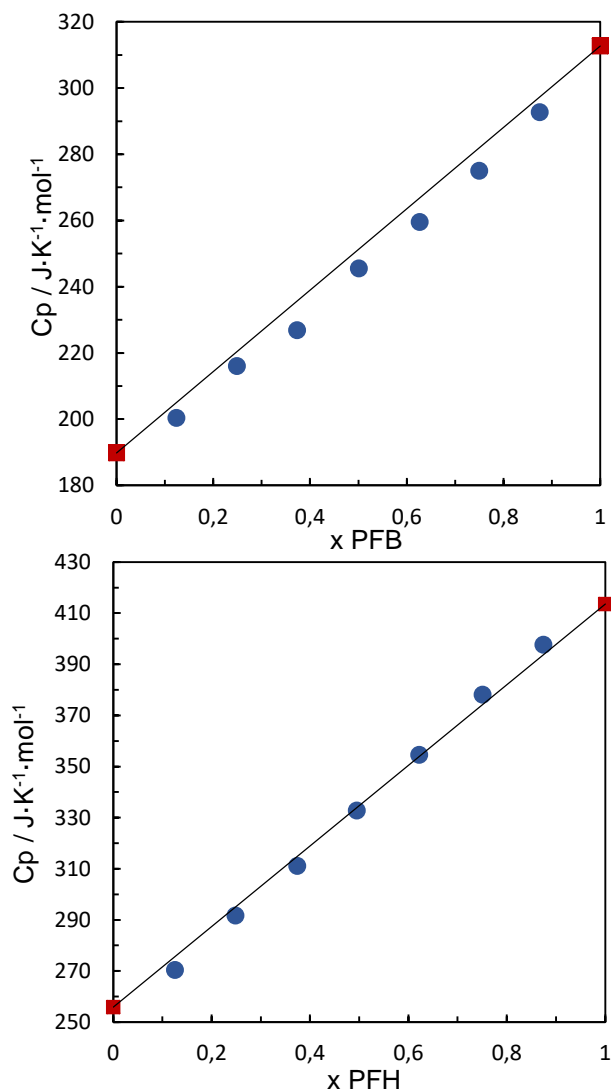


Figure 11 - Experimental values of Heat capacity as a function of the composition of the fluorocompound for pair Butanol + PFB (A) and Hexanol + PFH (B) at 313.15 K. The straight line represents the arithmetic mean of the pure compounds.

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 11, 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 12, 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.

As can be seen in Figure 12 A and B, the first pair of alcohols, Butanol + PFB, shows a negative deviation of the experimental values of  $Cp^E$  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.

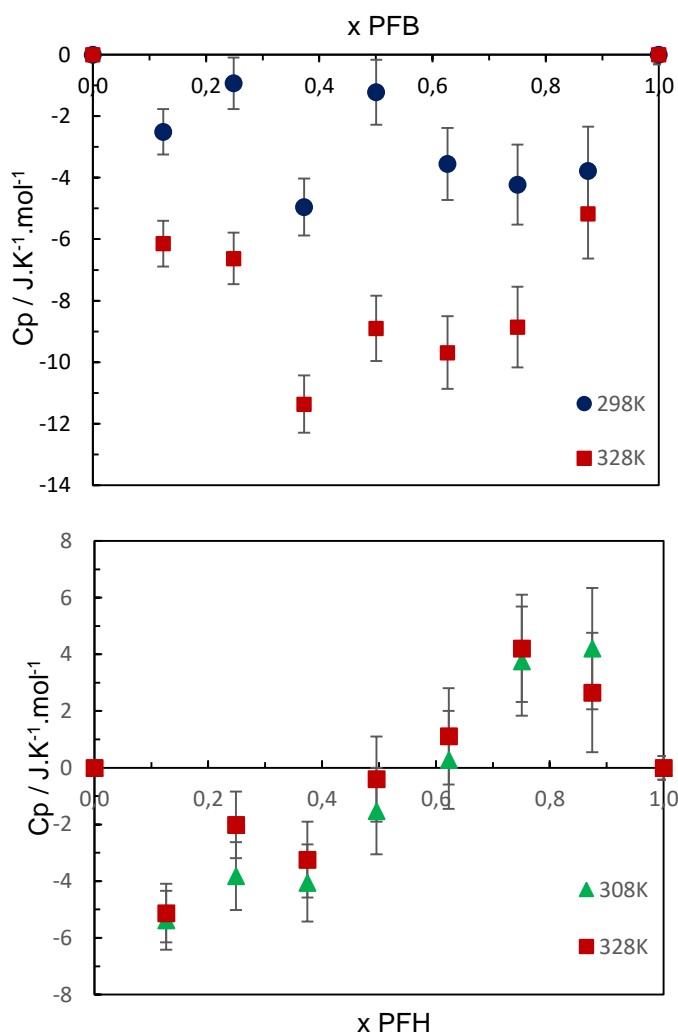


Figure 12 - Excess heat capacities as a function of composition of the fluorocompound at  $T=298,15\text{K}$  (●) and  $T=328,15\text{K}$  (■) for the pair Butanol + PFB (A) and at  $T=308,15\text{K}$  (▲) and  $T=328,15\text{K}$  (■) for the pair Hexanol + PFH (B).

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 (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 Cardyon<sup>TM</sup>, an innovative polymer using carbon dioxide (CO<sub>2</sub>) as raw material, the solubility of CO<sub>2</sub> in 2 different polycarbonates (PET-CO<sub>2</sub> 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 CO<sub>2</sub> 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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