Infinite dilution activity coefficient of solvents in poly-3-hydroxybutyrate from inverse gas chromatography

Anne C. Belusso , Maria Lina Strack , Lucas da S. Guadagnin , Débora J.L. Faccin , Nilo S.M. Cardozo , Rafael de P. Soares , Paula B. Staudt *

Federal University of Rio Grande do Sul, Chemical Engineering Department, Virtual Laboratory for Properties Prediction, Rua Ramiro Barcelos, 2777, CEP 90035-007, Porto Alegre, RS, Brazil

A B S T R A C T

Over the past few years, there has been an increase in the production of biopolymers, including poly(3-hydroxybutyrate) P(3HB). However, finding compatible solvents for these new materials can be a challenging task. The infinite dilution activity coefficient (IDAC) is a thermodynamic property that indicates the level of interactions between two substances and can be determined from experiments of inverse gas chromatography (IGC). In this work, IGC was used to determine IDAC of 12 solvents in P(3HB). The substances studied were 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), 1,2-dichloroethane, 2,2,2-trifluoroethanol, 2-butanone, 2-heptanone, benzene, chloroform, cyclohexane, dimethyl carbonate, ethyl acetate, isooctane and toluene. HFIP was found to be the most compatible solvent with P(3HB) with IDAC values smaller than 1. Isooctane presented the highest IDAC value, in agreement with the well known incompatibility between hydrocarbons and P(3HB). In addition, P(3HB) crystallinity was determined through IGC technique, enabling the calculation of the IDAC of amorphous phase only, where vapor-liquid equilibrium can be assumed. The degree of crystallinity obtained with HFIP analysis in P(3HB) was 68%, a value close to that previously reported in the literature.

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1. Introduction

The consumption of plastics, mainly in the form of disposable products, has highly increased in recent years. Non-biodegradable polymers, from petrochemical industry, have high resistance to degradation, a characteristic which has made them used in large scale [1,2]. As a result of this, concerns about solid waste management and environmental issues have grown worldwide. In this scenario, biopolymers are being increasingly studied as an alternative to common plastics. Amongst them, poly(3-hydroxybutyrate) (P(3HB)) is a strong candidate due to its biodegradability and also because it has mechanical properties similar to polypropylene [3,4]. Moreover, it can be produced by biological routes from renewable carbon sources derived from agriculture or industry [5].

However, there are several difficulties to overcome in order to allow the production of P(3HB) on a large scale [5,6]. The polymer

extraction from the culture medium is an important step of P(3HB) production, and a suitable solvent for P(3HB) is necessary, preferably environmentally friendly. In this context, the infinite dilution activity coefficient (IDAC) is an interesting property to study, since it indicates the level of interaction between two substances and how close to ideality a binary mixture is.

Among the existent techniques for measuring IDAC, the inverse gas chromatography (IGC) is an effective method for the study of solvents in polymers. In IGC, the material of interest is packed into the column to be used as stationary phase [7,8], and its interactions with different mobile phases are measured as different retention volumes. The study of polymers using this technique provides good approximation to conditions of processing and purification, opposed to methods that use dilute polymer solutions [9].

In available literature, there are many reports about the determination of IDAC in polymers and solvent mixtures using IGC [10—16]. All cited articles used similar procedures and materials to that used in this study. Lichtenthaler et al. [10] studied poly(dimethylsiloxane)-hydrocarbon systems; Galin and Rupprecht [11] investigated the thermodynamic interaction between linear or branched polystyrene and solutes, and also the adsorption

phenomena in IGC analyses; Schuster et al. [12] determined partial molar sorption and other mixing functions for polystyrene and non-polar solvents; Price et al. [13] measured thermodynamic data for several probe molecules in three polymers, poly(dimethylsiloxane) (PDMS), polyisobutylene (PIB) and ethylene-propylene rubber (EPR); Du et al. [14] investigated the interactions among 9 hydrocarbon polymers and 43 solvents; Zeng et al. [15] provided data of solvents in poly(vinyl alcohol) and cross-linked poly(vinyl alcohol) at several different temperatures; Papadopoulou and Panayiotou [16] calculated the thermodynamic properties of poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) in 15 solvents. However, to the best of our knowledge, just a few equilibrium data are available for biopolymers, and none for P(3HB).

Therefore, this research aims to obtain IDAC values for solvents in P(3HB) through the inverse gas chromatography technique. P(3HB) is used as stationary phase and various solvents as volatile samples in the inert mobile phase. Additionally, this research intends to study possible adsorption effects during IGC analysis due to P(3HB) polarity and to determine the polymer degree of crystallinity.

2. Methodology

2.1. Materials

Poly(3-hydroxybutyrate) (P(3HB)) was purchased from Sigma-Aldrich (Lot STBB9669V). The glass transition temperature and the melting point of P(3HB) are approximately 278 K and 453 K, respectively [4,17]. No data regarding molecular weight (M_w) was provided. Polar and nonpolar solvents were used as probes for IGC analysis. The solvents selection aimed at the study of biopolymer interactions with different chemical families, such as alkane, ketone, alcohol, esters, organic halides. Solvents known to be compatible with the polymer were chosen to be compared with other substances. This way a wide range of IDAC values was covered. Their information like boiling point, purity and supplier are listed in Table 1. All solvents were used without any further purification, as chromatographic methods separate any unwanted species on the column [18,19]. The support used for columns packing was Chromosorb P 80/100 mesh supplied by Manvilli.

2.2. Column preparation and inverse gas chromatography setup

Column packing containing from 20% to 25% (w/w) of the stationary phase (biopolymer) was prepared by coating the solid support, Chromosorb P, with a solution of 2,2,2-trifluoroethanol and P(3HB) at 343 K. The soaking method developed by Al-Saigh and Munk [20] was used. After complete 2,2,2-trifluoroethanol elimination in an oven at 343 K, thermogravimetric analyses were carried out in triplicate to confirm the polymer content using a TA Instruments SDT Q600 thermobalance with simultaneous thermal analyzers, differential scanning calorimetric and thermogravimetric (DSC/TGA). The average value was used with its standard uncertainty calculated according to Guide to the Expression of Uncertainty in Measurement (GUM) 21. The stainless steel column (0.6 m length and 4.57 mm internal diameter) was washed with soapy water, distilled water and rinsed with ethanol. After drying, the column was loaded with the coated support, and the weight of the packing material was estimated as a difference between packed and empty column mass, with an uncertainty of 5×10^{-08} kg. During column filling, vigorous manual agitation was applied to prevent dead/vacant volumes within the column. Column ends were filled with glass wool.

Five columns with different mass percent polymer loading were used: $19.28 \pm 0.15\%$, $23.26 \pm 0.03\%$, $21.04 \pm 0.06\%$, $26.71 \pm 1.08\%$ and $19.28 \pm 0.78\%$. Before the experiments, all columns were conditioned inside the chromatograph at 423 K under nitrogen flow until pressure stability, for at least 8 h. The equipment inlet pressure uncertainty was 0.0346 kPa and the uncertainty of atmospheric pressure was assumed to be 1 kPa.

Inverse gas chromatography experiments were carried out using a PerkinElmer Auto System XL Gas Chromatograph with a thermal conductivity detector (TCD). Injector and detector temperature were kept at 473 K during all analyses. As recommended in the literature, the minimum temperature used was defined to be at least 50 K above the polymer glass transition [22]. For all compounds listed in Table 1, analyses were performed using a column temperature range of 373 K–403 K, each 10 K with an uncertainty of 1 K. For HFIP, additional analysis were carried out from 403 K to 473 K, each 10 K, for the study of adsorption effects and polymer crystallinity. At each temperature and each column, injections were conducted in triplicate.

The carrier gas used was helium with a nominal flow rate defined in the chromatograph as 0.25 cm³/s (15 mL/min). The actual flow rate was measured using an Agilent ADM Flow Meter (Malaysia) with an uncertainty of 0.001667 cm³/s (0.1 mL/min). To determine only interactions between polymer and solvent, air was used as nonsorbing component [23].

The combined standard uncertainty was evaluated taking into account all uncertainties cited above [21]. Other variables were assumed to have negligible effect in the global uncertainty. The IGC technique applied in this work was validated for mixtures of polystyrene (PS) in different solvents, and the IDAC values obtained were in agreement with literature values [12,24] with deviations around 5%. These results can be found in Table S3 of Supplementary material.

Table 1
Source, purity and CAS-number of solvents used in this work.

Compounds	CAS No.	Boiling point (K)	Mass fraction purity	Supplier
1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)	920-66-1	331.35	0.99	Oakwood Products
1,2-dichloroethane	107-06-2	356.15	0.90	Vetec
2,2,2-trifluoroethanol	75-89-2	346.15	0.99	Fluka
2-butanone	78-93-3	353.15	0.99	Sigma-Aldrich
2-heptanone	110-43-0	423.15	0.99	Sigma-Aldrich
Benzene	1076-43-3	353.15	0.99	Merck
Chloroform	67-66-3	334.15	0.99	Synth
Cyclohexane	110-82-7	353.15	0.99	Synth
Dimethyl carbonate	616-38-6	363.15	0.99	Sigma-Aldrich
Ethyl acetate	141-78-6	350.15	0.99	Synth
Isooctane	540-84-1	372.15	0.99	Química Moderna Gold
Toluene	108-88-3	383.15	0.99	Dinàmica

Compounds boiling point and mass fraction purity data were provided by suppliers.

2.3. Theory

Retention time data were used to calculate the IDAC of tested solvents in P(3HB). At infinite dilution, interactions between the solvent molecules are avoided and solvent retention inside the column is mainly governed by interactions with the stationary phase [25]. The net retention volume (V_R) is calculated from the following equation [11,16]:

$$V_R = (t_R - t_M) J_2^3 \frac{T}{T_a} Q \tag{1}$$

where t_R and t_M are the retention times of solvent and air, respectively, Q is the carrier gas flow rate measured at column outlet pressure (atmospheric pressure) P_{out} and room temperature T_a, T is the column temperature and J_2^3 is the James and Martin factor used to correct carrier gas compressibility, defined as [26]:

$$J_2^3 = \frac{3}{2} \left[\frac{\left(\frac{P_{in}}{P_{out}}\right)^2 - 1}{\left(\frac{P_{in}}{P_{out}}\right)^3 - 1} \right] \tag{2}$$

where P_{in} and P_{out} are column inlet and outlet pressure, respectively.

The specific retention volume (V_g^0) is the property used to obtain several thermodynamic properties from IGC and it is calculated in terms of V_R as [8,16]:

$$V_g^0 = \frac{V_R T_{273.15}}{m_p T} \tag{3}$$

where $T_{273.15}$ is the temperature of 273.15 K and m_p is the polymer weight inside the column.

When studying polymers, the mass-based infinite dilution activity coefficient (Ω^∞) is more convenient than the molar quantity (γ^∞) because polymer molecular weight can be unknown or poorly defined [27]. Based on vapor−liquid equilibrium achieved during the IGC analysis between polymer (liquid − stationary phase) and solvent (vapor − mobile phase) Ω^∞ is calculated by Refs. [23,28]:

$$\Omega^\infty = \frac{R T_{273.15}}{V_g^0 M_1 f_1} \tag{4}$$
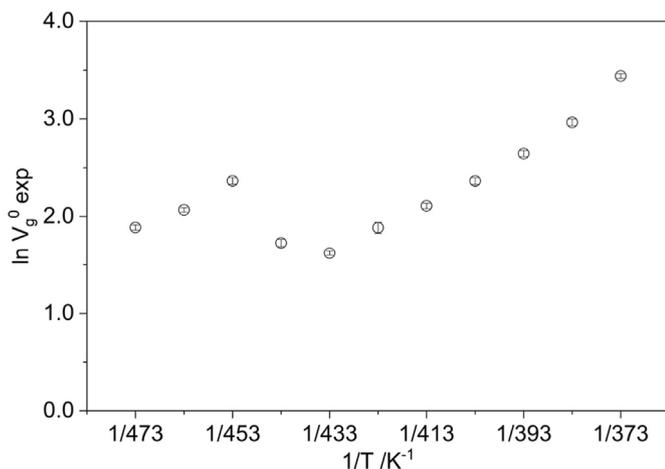
Fig. 1. Retention diagram for HFIP in the temperature range of 373 K−473 K.

where R is the universal gas constant, M_1 is the solvent molecular mass and f_1 is solvent fugacity coefficient [29]:

$$f_1 = P_1^{sat} exp \left(\frac{P_1^{sat} \left(B_{11} - v_1^l \right)}{RT} \right) \tag{5}$$

being $P1^{sat}$ the solvent vapor pressure at temperature T; B_{11} its pure second virial coefficient, that can be obtained from correlations available in the literature [30]; and v_1^l the solvent liquid molar volume. Sources and values of B_{11} and v_1^l used in this study are presented as Supplementary material.

However, when using IGC for crystalline and/or polar stationary phases, like P(3HB), interactions other than only VLE must be taken into account and corrected values of retention volume must be applied to Equation (4). Due to the relevance of these effects in the present study they are further discussed in the following sections.

2.3.1. Adsorption contribution

The specific retention volume (V_g^0) experimentally obtained is represented by sum of two contributions [31]:

$$V_g^0 = V_{gb}^0 + V_{g_{ads}}^0 \tag{6}$$

where, V_{gb}^0 is the retention volume regarding vapor−liquid(polymer) interactions, generally called as the bulk contribution; and $V_{g_{ads}}^0$ is the retention volume due to physical surface adsorption, which includes vapor adsorption in the inert solid, in the polymeric crystals and in the liquid layer.

According to Galin and Rupprecht [11] and Courval and Gray [32], Equation (6) can be rewritten as

$$V_g^0 = V_{gb}^0 + K_a \left(\frac{S}{w} \right) \tag{7}$$

with K_a representing adsorption contributions in the analysis, S the column inert support weight and w the polymer weight. As only bulk contributions should be taken into account for Ω^∞ determination, V_{gb}^0 can be obtained by the linear coefficient of a regression of experimental V_g^0 and the quantity $\frac{S}{w}$ measured using at least three columns with different polymer loading. In a plot of V_g^0 versus $\frac{S}{w}$, the lower the slope of experimental data, the smaller is the surface adsorption contribution tending to a horizontal line for nonpolar amorphous polymers.

It is important to mention that surface contribution vary according to the pair polymer/solvent. For a polar stationary phase, such as P(3HB), adsorption contribution can be significant since both nonpolar and polar solvents can present high adsorption in polar stationary phases [9,31].

2.3.2. Degree of crystallinity

IGC technique is a way of determining crystallinity of the stationary phase. Braun and Guillet [33] showed that the crystallinity fraction (X_c) is obtained by comparing retention volumes measured below T_m (V_g^0) and linear extrapolation of retention volumes measured above the melting temperature ($V_g^{0'}$), according to the equation:

$$X_c = 1 - \left(\frac{V_g^0}{V_g^{0'}} \right) \tag{8}$$

To determine P(3HB) crystallinity, analyses above its melting
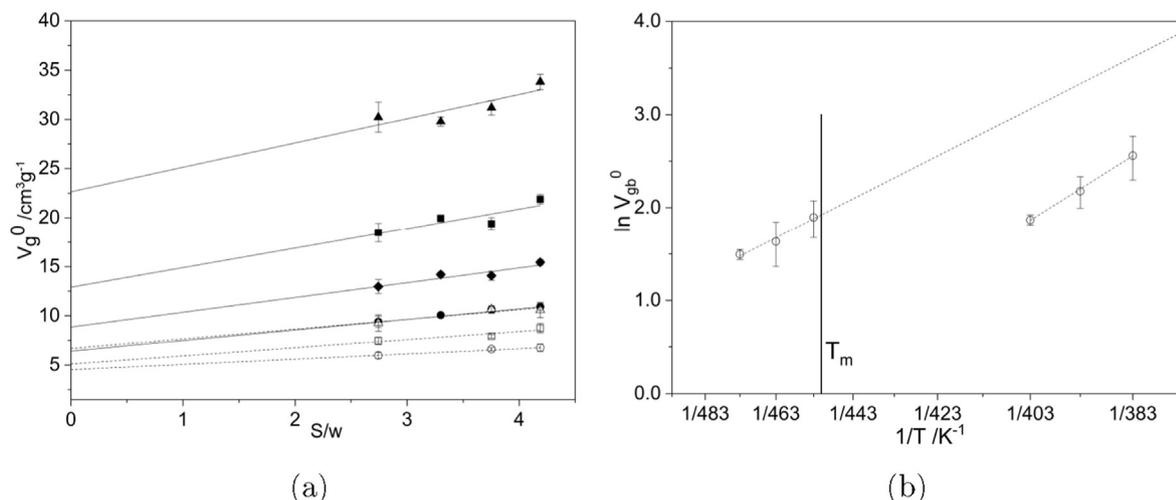
Fig. 2. (a) Specific retention volume versus Chromosorb/polymer weight for temperatures above and below P(3HB) T_m. (▲ 373 K, ■ 383 K, ◆ 393 K, · 403 K △ 453 K, □ 463 K, ○ 473 K) (b) Retention diagram of bulk contribution for HFIP in P(3HB) above and below T_m with extrapolated lines for V_{gb}^0 estimation.

Table 2
Experimental retention volumes calculated for different solvents at 373 K and 383 K.

Compounds	373 K			383 K		
	V_g^0 exp.	V_{gb}^0	V_{gb}^0 amorphous	V_g^0 exp.	V_{gb}^0	V_{gb}^0 amorphous
HFIP	31.24 ± 2.40	22.63 ± 3.96	69.98 ± 13.00	19.92 ± 1.58	12.91 ± 2.97	39.92 ± 9.17
1,2-dichloroethane	12.02 ± 1.13	5.64 ± 1.36	17.45 ± 4.19	8.71 ± 0.78	4.87 ± 1.0	15.05 ± 5.27
2,2,2-trifluoroethanol	12.77 ±1.12	6.70 ± 1.45	20.72 ± 4.47	8.60 ± 0.67	5.76 ± 1.14	17.82 ± 3.53
2-butanone	7.38 ±0.71	5.02 ± 0.40	10.20 ± 3.92	5.32 ± 0.43	3.40 ± 0.90	10.51 ± 2.78
2-heptanone	41.42 ±3.58	27.50 ± 1.10	85.02 ± 3.41	28.78 ± 2.63	14.44 ± 4.22	44.65 ± 13.04
Benzene	7.58 ± 0.73	3.42 ± 1.37	10.58 ± 2.65	5.50 ± 0.50	2.70 ± 1.03	8.35 ± 2.42
Chloroform	7.65 ± 0.49	6.35 ± 0.79	19.62 ± 2.45	5.66 ± 0.42	4.22 ± 0.95	13.04 ± 2.94
Cyclohexane	3.52 ± 0.37	1.43 ± 0.78	4.43 ± 2.41	2.73 ± 0.23	1.51 ± 0.24	4.66 ± 0.75
Dimethyl carbonate	10.00 ± 0.98	4.33 ± 2.00	13.38 ± 6.18	7.32 ± 0.61	4.41 ± 1.20	13.63 ± 3.72
Ethyl acetate	6.29 ± 0.66	2.60 ± 1.31	8.05 ± 4.06	4.52 ± 0.34	3.54 ± 0.88	10.96 ± 2.71
Isooctane	3.60 ± 0.41	0.95 ± 0.68	2.95 ± 2.10	2.79 ± 0.26	1.32 ± 0.41	4.07 ± 1.28
Toluene	13.47 ± 1.21	7.88 ±0.28	24.37±0.87	10.15±0.90	5.60±1.99	17.33±6.16

Standard uncertainty u(T) = 1 K.
Values after ± correspond to expanded uncertainties, calculated with a coverage factor k = 2.

Table 3
Experimental retention volumes calculated for different solvents at 393 K and 403 K.

Compounds	393 K			403 K		
	V_g^0 exp.	V_{gb}^0	V_{gb}^0 amorphous	V_g^0 exp.	V_{gb}^0	V_{gb}^0 amorphous
HFIP	14.16 ± 1.11	8.82 ± 1.47	27.27 ± 4.53	10.25 ± 0.78	6.48 ± 0.35	20.03 ± 1.09
1,2-dichloroethane	6.86 ± 0.62	3.62 ± 1.06	11.18 ± 3.28	5.53 ± 0.47	2.90 ± 0.58	8.96 ± 1.79
2,2,2-trifluoroethanol	6.60 ± 0.56	3.63 ± 0.70	11.23 ± 2.17	5.18 ± 0.43	2.88 ± 0.36	8.90 ± 1.11
2-butanone	4.34 ± 0.34	2.98 ± 0.72	9.21 ± 2.22	3.51 ± 0.30	1.78 ± 0.08	5.49 ± 0.25
2-heptanone	20.72 ± 1.93	10.67 ± 4.38	33.00 ± 13.54	15.41 ± 1.42	6.58 ± 0.86	20.33 ± 2.66
Benzene	4.50 ± 0.41	2.15 ± 0.71	6.63 ± 1.69	3.74 ± 0.33	1.75 ± 0.04	5.42 ± 0.51
Chloroform	4.51 ± 0.37	3.28 ± 0.96	10.15 ± 2.97	3.73 ± 0.31	2.05 ± 0.19	6.34 ± 0.58
Cyclohexane	2.27 ± 0.20	1.10 ± 0.20	3.41 ± 0.63	1.90 ± 0.19	0.67 ± 0.03	2.08 ± 0.08
Dimethyl carbonate	5.62 ± 0.49	3.23 ± 1.08	9.98 ± 3.33	4.64 ± 0.40	2.36 ± 0.32	7.30 ± 1.00
Ethyl acetate	3.53 ± 0.32	1.89 ± 0.69	5.84 ± 2.13	2.94 ± 0.25	1.57 ± 0.15	4.86 ± 0.48
Isooctane	2.21 ± 0.21	0.90 ± 0.25	2.79 ± 0.77	1.84 ± 0.17	0.78 ± 0.09	2.41 ± 0.27
Toluene	7.82 ± 0.72	3.65 ± 1.19	11.27 ± 3.68	6.34 ± 0.57	2.84 ± 0.43	8.78 ±1.34

Standard uncertainty u(T) = 1 K.
Values after ± correspond to expanded uncertainties, calculated with a coverage factor k = 2.

temperature were carried out at 453 K, 463 K and 473 K, using HFIP in the mobile phase. Such narrow temperature range was used to avoid P(3HB) degradation inside the column, expected to be around 473 K, very close to its melting point. Only HFIP was used in this step because it has well known better compatibility with P(3HB).

Chen and Al-Saigh [34] and Camacho et al. [35] also suggested the use of compatible solvents for experiments with poly(vinylidene fluoride), and polyethylene and EVA copolymers, respectively. In order to confirm the constant polymer mass inside the column, column weight was checked before and after experiments.
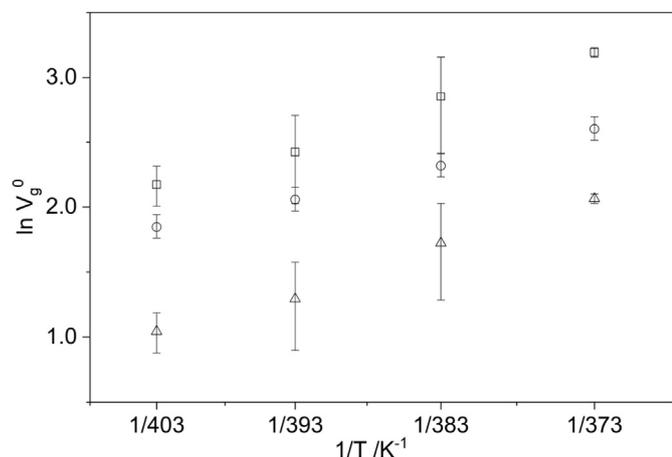
Fig. 3. Retention diagram for toluene. ○ experimental; △ only bulk contribution; ▫ bulk contribution with amorphous P(3HB).

3. Results and discussion

3.1. Degree of crystallinity

When using IGC for polymers studies, with the polymer like stationary phase, one can expect a sharp transition in the retention diagram around its melting point. In this work, it was possible to see such behavior for P(3HB) using HFIP as probe as shown in Fig. 1.

Retention data above and below P(3HB) melting temperature were fitted to Equation (7) and can be seen in Fig. 2 (a). Correlation, angular and linear coefficients data of Fig. 2(a) are presented in Table S2 of Supplementary material.

As can be seen in the results of Fig. 2(a), adsorption influence is observed in the whole temperature range analyzed. Experimental data slopes (K_a) are higher than 10% of linear coefficients (V_{gb}^0) showing that adsorption between stationary and mobile phase is relevant in this investigation and must be disregarded in order to calculate crystallinity degree.

Using V_{gb}^0 values, crystallinity of P(3HB) was calculated with Equation (8). The extrapolation performed for $V_{gb}^{0'}$ estimation is illustrated in Fig. 2(b) and a crystallinity fraction value of 0.68±0.08 was obtained in the temperature range analyzed. This result was expected since P(3HB) has a well known high crystallinity degree [36−38].

3.2. Specific retention volume

Experimental retention volumes for all analyzed solvents were calculated using Equation (3). Retention volumes of bulk contribution (V_{gb}^0) were obtained through linear data regression of Equation (7). In order to take into account only interactions between vapor and liquid amorphous polymer, P(3HB) mass inside the column was determined subtracting the crystalline portion of

Table 4
Experimental IDAC in weight fraction (Ω^∞) for solvents in P(3HB) at 373 K and 383 K.

Compounds	373 K			383 K		
	Ω^∞ exp.	Ω_b^∞	Ω_b^∞ amorphous	Ω^∞ exp.	Ω_b^∞	Ω_b^∞ amorphous
HFIP	1.09 ± 0.09	1.50 ± 0.26	0.48 ± 0.09	1.32 ± 0.11	2.02 ± 0.46	0.65 ± 0.15
1,2-dichloroethane	12.10 ± 1.25	25.58 ± 6.15	8.27 ± 1.99	12.81 ± 1.28	22.75 ± 7.96	7.36 ± 2.57
2,2,2-trifluoroethanol	7.17 ± 0.67	13.58 ± 2.93	4.39 ± 0.95	7.81 ± 0.67	11.62 ± 2.30	3.76 ± 0.74
2-butanone	24.10 ± 2.44	35.15 ± 2.77	17.30 ± 6.64	25.63 ± 2.24	39.93 ± 10.55	12.92 ± 3.41
2-heptanone	26.97 ± 2.30	36.57 ± 1.47	11.83 ± 0.47	27.43 ± 2.40	48.88 ± 14.28	15.81 ± 4.62
Benzene	22.89 ± 2.39	50.33 ± 20.10	16.28 ± 4.08	24.53 ± 2.50	49.59 ± 18.87	16.04 ± 4.64
Chloroform	8.55 ± 0.60	10.28 ± 1.28	3.33 ± 0.41	9.14 ± 0.72	12.22 ± 2.75	3.95 ± 0.89
Cyclohexane	47.57 ± 5.20	115.71 ± 63.10	37.43 ± 20.41	47.68 ± 4.36	86.06 ± 13.83	27.84 ± 4.47
Dimethyl carbonate	19.25 ± 2.03	44.07 ± 20.35	14.26 ± 6.58	19.76 ± 1.77	32.63 ± 8.90	10.55 ± 2.88
Ethyl acetate	21.56 ± 2.34	51.60 ± 26.05	16.69 ± 8.43	22.95 ± 1.79	29.15 ± 7.22	9.43 ± 2.33
Isooctane	57.97 ± 7.14	215.83 ± 153.70	69.81 ± 49.72	57.31 ± 5.66	120.39 ± 37.87	38.94 ± 12.25
Toluene	25.76 ± 2.60	43.78 ± 1.57	14.16 ± 0.51	25.69 ± 2.47	46.23 ± 16.44	14.95 ± 5.32

Standard uncertainty u(T) = 1 K.
Values after ± correspond to expanded uncertainties, calculated with a coverage factor k = 2.

Table 5
Experimental IDAC in weight fraction (Ω^∞) for solvents in P(3HB) at 393 K and 403 K.

Compounds	393 K			403 K		
	Ω^∞ exp.	Ω_b^∞	Ω_b^∞ amorphous	Ω^∞ exp.	Ω_b^∞	Ω_b^∞ amorphous
HFIP	1.46 ± 0.13	2.33 ± 0.39	0.75 ± 0.13	1.62 ± 0.14	2.56 ± 0.14	0.83 ± 0.04
1,2-dicloroethane	12.69 ± 1.25	23.91 ± 7.01	7.74 ± 2.27	12.49 ± 1.24	23.65 ± 4.72	7.65 ± 1.53
2,2,2-trifluorethanol	7.69 ± 0.71	13.89 ± 2.69	4.49 ± 0.87	7.54 ± 0.69	13.49 ± 1.68	4.36 ± 0.54
2-butanone	24.58 ± 2.03	35.66 ± 8.58	11.53 ± 2.78	24.21 ± 2.33	47.57 ± 2.19	15.38 ± 0.71
2-heptanone	27.33 ± 2.43	47.52 ± 19.49	15.37 ± 6.30	27.75 ± 2.55	56.58 ± 7.41	18.30 ± 2.40
Benzene	23.74 ± 2.41	49.38 ± 16.30	15.97 ± 4.07	22.88 ± 2.33	48.56 ± 1.18	15.71 ± 1.49
Chloroform	9.20 ± 0.78	12.59 ± 3.69	4.07 ± 1.19	9.04 ± 0.83	16.40 ± 1.51	5.30 ± 0.49
Cyclohexane	45.77 ± 4.41	93.44 ± 17.27	30.22 ± 5.59	44.31 ± 5.01	123.81 ± 4.64	40.05 ± 1.50
Dimethyl carbonate	19.78 ± 1.91	34.24 ± 11.43	11.08 ± 3.70	18.75 ± 1.85	36.59 ± 4.99	11.84 ± 1.61
Ethyl acetate	23.05 ± 2.20	42.86 ± 15.61	13.86 ± 5.05	22.07 ± 2.04	40.99 ± 4.03	13.26 ± 1.30
Isooctane	56.66 ± 5.94	137.85 ± 38.15	44.59 ± 12.34	54.30 ± 5.61	126.98 ± 14.19	41.07 ± 4.59
Toluene	25.54 ±2.68	54.35±17.75	17.58±5.74	24.49±2.56	54.29 ± 8.31	17.56±2.69

Standard uncertainty u(T) = 1 K.
Values after ± correspond to expanded uncertainties, calculated with a coverage factor k = 2.
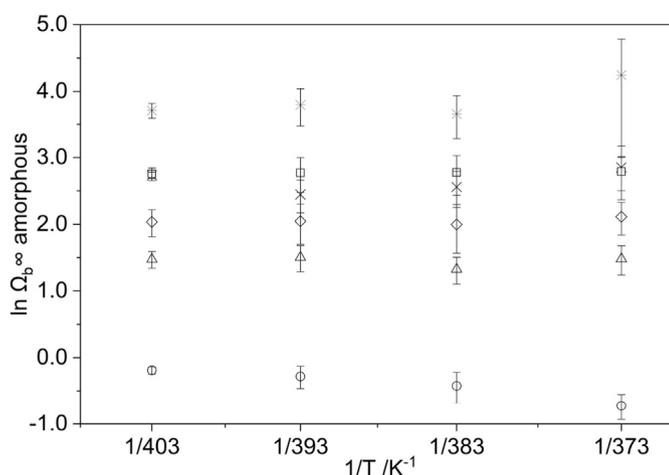
Fig. 4. Natural logarithm of Ω_b^∞ amorphous as a function of temperature for ∘ HFIP, Δ 2,2,2-trifluorethanol, ⋄ 1,2-dichloroethane, × 2-butanone, □ benzene and isooctane in P(3HB).

the total mass [34], considering a crystallinity degree of 68%. All retention volumes along with experimental expanded uncertainties, are listed in Tables 2 and 3. Small retention volumes indicate high IDAC values and, consequently, lower compatibility between the solvent and P(3HB).

As can be observed, significant smaller values of V_{gb}^0 are obtained when compared to raw experimental ones, indicating an important adsorption contribution for all chemicals investigated [31]. Disregarding the crystalline polymer inside the column, retention volumes increase considerably due to the smaller polymer amount available to interact with solvent molecules. The retention volume values in Tables 2 and 3 for toluene can be visually compared in Fig. 3.

3.3. Infinite dilution activity coefficients − Ω^∞

IDAC values were determined using Equation (4) at 373 K, 383 K, 393 K and 403 K. Results for twelve solvents are listed in Tables 4 and 5.

High IDAC values indicate that the mixture of P(3HB) and solvent exhibit a strong positive deviation from the Raoult's law, while low values of IDAC mean strong compatibility and interactions. According to Açikses et al. [39] IDAC values less than 5, indicate good compatibility between polymer and solvent. Such fact was observed in this work for organohalogenates (HFIP, 1,2-dichloroethane, 2,2,2-trifluorethanol and chloroform) for all temperatures studied, being HFIP most compatible with P(3HB). Isooctane presented the highest IDAC value among all analyzed substances.

Fig. 4 shows the IDAC natural logarithm of six solvents in amorphous P(3HB) as a function of inverse absolute temperature. These solvents present different structures and interactions with P(3HB), and also an increase in IDAC values with a decrease in solvent polarity. The natural logarithm of Ω_b^∞ amorphous for these solvents did not significantly vary with temperature.

It is worth noting that despite the low IDAC values for organohalogenates solvents, the dissolution of P(3HB) only occurs for high solvent-polymer ratios, since the high polymer crystallinity degree contributes to the decrease in solubility, even when using compatible solvents [40,41].

4. Conclusion

Values of infinite dilution activity coefficients (IDAC) were successfully determined for twelve selected compounds in poly(3-hydroxybutyrate) P(3HB) at four different temperatures (373 K−403 K) by inverse gas chromatography (IGC). It has been found that IDAC values mostly depend on the substances polarity and structure. Orgagnohalogenates showed greater compatibility with P(3HB) and smaller IDAC values, with 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) being the solvent with the lowest IDAC value at all temperatures analyzed. As expected, alkanes presented higher IDAC values, showing that nonpolar compounds have low compatibility with P(3HB). The adsorption phenomena proved to be important for the calculation of IDAC. Inverse gas chromatography was also used to determine the degree of crystallinity of P(3HB) in the stationary phase, the value found for pair P(3HB)−HFIP was 68%. The high crystallinity of P(3HB) reported in the literature was confirmed in this work.

CRediT authorship contribution statement

Anne C. Belusso: Conceptualization, Investigation, Formal analysis, Writing - original draft. **Maria Lina Strack:** Conceptualization, Methodology, Validation, Investigation, Writing - original draft. **Lucas da S. Guadagnin:** Conceptualization, Methodology. **Débora J.L. Faccin:** Conceptualization, Resources. **Nilo S.M. Cardozo:** Conceptualization, Resources. **Rafael de P. Soares:** Conceptualization, Writing - review & editing. **Paula B. Staudt:** Conceptualization, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fluid.2020.112742.

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