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# Characterization of biodegradable polymers by inverse gas chromatography: Blends of amylopectin and poly (3-hydroxybutyric acid)

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## ABSTRACT

Using the Inverse Gas Chromatography Method (IGC), the morphology, surface energy, degree of crystallinity and the thermodynamics of 27 solutes with blends of amylopectin (AP) and poly (3-hydroxybutyric acid) (PHBA) were investigated at a range of 80-120 °C. The strength of the interactions of three compositions of AP-PHBA blends was investigated. The effect of the chemical nature of solutes on the thermodynamic quantities was eliminated. The effect of various compositions of the blend on these quantities was also explored. Retention diagrams of semi-crystalline AP blended with amorphous PHBA enabled the estimation of the melting temperature, $T_m$, of AP in the blend. IGC showed a modest affinity of AP, as a host, to PHBA as a diluent polymer. This observation was complemented by the degree of crystallinity and the dispersive component of surface energy. The degree of crystallinity was significantly reduced when AP was blended with three weight fractions of PHBA, which led to a depression in AP's $T_m$ values. This was complemented by the dispersive component of the surface energy of AP, it was reduced by the blending process.

**KEYWORDS:** poly (3-hyudroxybutyric acid), amylopectin, inverse gas chromatography, degree of crystallinity, surface energy, interaction coefficients, differential scanning calorimetry, X-ray diffraction, polymer-polymer interaction, entropy of mixing.

## 1. INTRODUCTION

In an effort to characterize polymer blends containing biodegradable polymers, we extend our recent studies published in several journals [1-5] to include a blend of amylopectin (AP) and poly (3-hydroxybutyric acid) (PHBA). Recently, we reported the morphology changes, surface energy, crystallinity and the thermodynamics of a series of polymer blends containing starch (AP) using the inverse gas chromatography method (IGC) [1-5]. The significance of blending a pair of biodegradable polymers stems from the fact that most biodegradable polymers are mechanically weak and their physico-chemical properties can be improved by the blending process. We showed that blending starch with a biodegradable polymer improved the starch's physico-chemical properties [5]. Understanding these properties brings more attention to improving the blends' chemical and physical properties which eventually increases their application in industry, medical science and treatment of plastic waste. Amylopectin as a starch and its blends have attracted much attention as environmentally biodegradable polymers [6-13]. In particular, a blend containing PHBA is of interest due to its biodegradability and availability from naturally renewable resources. Bacteria decompose PHBA into water and carbon dioxide under environmental conditions. PHBA offers

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Fifth in the series of articles published by the authors, regarding biodegradable polymer characterization.

many advantages over traditional petrochemically derived plastics. It possesses better physical properties than polypropylene for food packaging applications and is completely nontoxic.

The thermal behavior and phase morphology of starch-blend systems have been studied by many techniques; among these are: differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy, solvent extraction, X-ray diffraction, optical rotation, nuclear magnetic resonance (NMR) and polarizing optical microscopy [14-17]. The morphology and compatibility of blends of a variety of biodegradable polymers and poly (3-hydroxybutyrate) (PHB) have also been studied using the above techniques [8, 18-23]. IGC has not been applied for the characterization of starch-PHBA.

It is our intention in this paper to expand the range of experimental techniques to include inverse gas chromatography (IGC). When two polymers are mixed to form a polymer blend, the resulting mixture is enormously viscous. Experimental techniques developed for dilute solution studies are often inapplicable under these conditions. Furthermore, some polymers are insoluble, or partially soluble in known solvents and hence dilute solution techniques cannot be applied. IGC (sometimes called the molecular probe technique) eliminates both of these difficulties. IGC method is based on the principles of conventional gas chromatographic instrument which provides the following features: reasonable cost, experimental simplicity, and the ease of operation with large amounts of data can be collected. Therefore, IGC is becoming the method of choice for the study of thermodynamic interactions of small molecules with polymers in the solid phase. It can also be used to measure surface areas and adsorption isotherms, glass and other solid phase transitions in polymers, degrees of crystallinity, crosslink density and diffusion constants for small molecules in polymeric materials. Since 1969, inverse gas chromatography (IGC) has been used for the characterization of polymers, blends and materials. During this period, it has undergone extensive development and received considerable interest for its application in polymers and blends [1-5, 13-21]. The IGC technique utilizes conventional gas chromatography, with minor modifications, to measure the interaction between pure solute (mobile phase) and the polymers or blends (stationary phase) in terms of the retention time of the solute. The term “solute” is used to represent the low-molecular weight volatile solvent that is usually injected into the chromatographic column. Solute is dispersed in a mobile phase and the polymer blend is stationary in the column as a liquid phase. Volatility of solutes ensures the availability of a vanishingly small amount of solute in the mobile phase which leads to a fast establishment of equilibrium between the gas and the stationary phase. The term “inverse” refers to the fact that the stationary phase (the polymeric system) is under study in the IGC experiments, in contrast to the objective of the separation of components in traditional gas chromatography (GC). The stationary phase is prepared by dissolving the polymer or polymer blend in the appropriate solvent and depositing the resulting mixture onto a solid support using a specific technique developed by us [22]. There are excellent reviews on the IGC method, outlining the methodology and technique, given by Guillet and colleagues [15, 16], Munk [17], Al-Saigh [5, 14], and Al-Saigh and Guillet [23].

To improve starch-based polymers’ physico-chemical properties, blending of a pair of natural polymers will be attempted in this proposal. Special attention will be devoted to the surface, physical, and the chemical properties of the new blends. The blending process is strongly influenced by the properties of the components and the interface. In the absence of chemical bonding within the blend, the strength of dispersive and acid-base interaction forces is essential for the adhesion between the components. We will show that IGC is capable of providing a wealth of information on AP-PHBA blend. Its analysis will reflect on the morphology changes with the following: temperature, the compatibility (solubility) of blends at different compositions and temperatures in terms of thermodynamics, and its relationship with $T_m$ and $T_g$, crystallinity, and surface energy. Since amylopectin is a semi-crystalline polymer and the degree of crystallinity is expected to change when it is blended with another biodegradable polymer, IGC has the advantage over the DSC method in measuring the degree of crystallinity at each individual temperature. That will prove its versatility as compared to the DSC method. The thermodynamic calculations derived from the measured chromatographic quantities will reveal the strength of the interactions between the polymer pair (AP-PHBA) at a range of weight fractions and temperatures. It will also reveal the strength of the interaction of 27 solutes that have different chemical nature, with the polymer pair.

## 2. THERMODYNAMICS OF IGC

The thermodynamics of IGC has been derived and reviewed in a series of our publications [1-5], one of which was published elsewhere [1]. Since the goal of this paper is to obtain information on several aspects of the physico-chemical properties of AP-PHBA blends, we will divide this section into several sub-categories.

### 2.1. Interaction parameters (Appendix A)

Since a blend of AP-PHBA is a ternary system, IGC is capable of obtaining two different interactions: 1) interaction of the mobile phase probed by 27 solutes with the blend is designated as $\chi_{1\text{-blend}}$ (subscripted '1' refers to the solute and 'blend' to the pair of polymers). 2) the interaction within the polymer pair itself designated as $\chi_{23}'$ (subscripted '2' and '3' refer to the polymers 1 and 2, respectively). The derivations of both $\chi_{1\text{-blend}}$ and $\chi_{23}'$ are illustrated in Eqns. (A11) and (A15).

### 2.2. Dispersive surface energy

The total surface energy of AP-PHBA is the combination of several contributions depending on the nature of the solute that is interacting with the polymer surface. One of these contributions is due to the dispersive interaction forces such as those in alkanes. The dispersive forces in alkanes increase as more $CH_2$ group is added to its backbone. If the solute used exhibits acid-base interaction forces, it also contributes to the total value of the surface energy. When the mobile gaseous phase comes in contact with the polymeric surface, an interfacial energy will be created according to the nature of the interacting solute and whether it is polar ($\gamma_p$) and/or non-polar or dispersive ($\gamma_d$). Then, the adsorption of the solute vapor onto the polymer surface will be affected by the magnitude of the surface free energy. Since the alkane series used in this work has a uniform increase in dispersive forces, it makes it possible to calculate the dispersive component of the surface energy of AP-PHBA using IGC. From the measured chromatographic quantities which lead to the calculation of $V_g^o$, the dispersive component of the surface energy of AP-PHBA blends ($\gamma_s^d$) at various compositions can be calculated. A complete theoretical treatment for the calculation of $\gamma_s^d$ was first published by Fowkes [24]. $V_g^o$ from Eqn. (A4) can be utilized in the calculation of the equilibrium constant K between the adsorbed solute and the polymer surface and the free energy of adsorption of vapor on the polymer surface, $\Delta G_1^s$, as follows:

$$\Delta G_1^s = -RT \ln V_g^o + C \tag{1}$$

Eqn. (1) relates the free energy of adsorption to the polymers' surface as follows:

$$RT \ln V_g^o + C = 2Na\sqrt{\gamma_s^d \gamma_i^d} \tag{2}$$

$\gamma_s^d$ and $\gamma_i^d$ are the dispersive components of the solid surface and the interactive solutes phase, respectively. Eqn. (2) can be rewritten to yield the dispersive surface energy as follows:

$$\gamma_s^d = \left[\frac{1}{4\,\gamma_{CH_2}}\right]\left[\frac{(\Delta G_a^{CH2})^2}{(N.\,a_{CH_2})^2}\right] \tag{3}$$

where $\gamma_{CH2}$ is the surface energy of a hydrocarbon consisting only of n-alkanes, $a_{CH2}$ is the area of one $-CH_2$ group. Eqn. (3) will be routinely used to obtain the dispersive surface energy of polymers.

## 3. MATERIALS AND METHODS

### 3.1. Materials

Amylopectin (AP) with a molar mass of 6.60 x $10^6$ gram/mol, was purchased from Sigma-Aldrich, USA, as potato starch. It contains 25% amylase. Poly (3-hydroxybutyric acid) (PHBA) was purchased from Sigma-Aldrich, USA, as a polydisperse polymer with an average $M_W \approx 65676$ gram/mol as determined by GPC, relative to polystyrene standard (10 x $10^3$ to 8.4 x $10^6$ g/mol). Analysis was performed on Shimadzu LC-20AD GPC. The sample was eluted with chloroform with a flow rate of 1.0 ml/min at 35 °C. The eluted compounds were monitored by a Shimadzu RID-10A refractive index detector. Shimadzu auto sampler was used (SIL-20A) for all injections of 50 µL each. The whole system was powered by Shimadzu LCsolution software.

A series of families of solvents called “solutes”, each having a different chemical nature was selected to interact with the blends of AP-PHBA. A total of 27 chromatographic grade solutes representing six families such as alkanes, acetates, oxy group, ether and ketones, halogenated and six-member ring were used. Each solute was assigned a code to allow easy programming for the calculations of molar volume, saturated vapor pressure, gas and liquid densities and $B_{11}$ parameter according to our earlier publications [13, 18-22]. Each family has a different chemical nature from the other depending on the functional groups and polarity. This selection was necessary to test whether the thermodynamics of polymers and polymer blends are dependent on the nature of the solute groups used. For example, the alkane family reveals the effect of its dispersive forces on the interactions with the pure homo polymers and the blends. Acetates will reveal the effect of dipole-dipole and H-bonding interactions; halogenated, and ether and ketones families will reveal the effect of H-bonding interactions. The six-membered ring group will reveal the effect of Van der Waal’s interactions on the solubility of these polymers. These solutes exhibit different interactions with the stationary phase that will reveal how the different chemical nature of the injected solutes affect the thermodynamic parameters obtained in this work: $\chi_{12}$, $\chi_{13}$, $\chi_{1\text{-blend}}$ and $\chi_{23}'$ of homopolymers and their blends. All 27 solutes were purchased from Sigma-Aldrich, USA as chromatographic grade. Their purity was checked by gas chromatography prior to use. An inert chromatographic support, Chromosorb W (AW-DMCS treated, 60/80 mesh) was obtained from Resteck.

### 3.2. Instrumentation and procedure

A complete description of the instrumental set-up was outlined in our publication elsewhere [1]. Chromatographic measurements were made using an IGC station, consisting of a Shimadzu GC2014. The chromatograph was equipped with a thermal conductivity detector, and was modified to minimize the instrumental artifacts in the measurement of the chromatographic quantities used in Eqn. (A4), such as the carrier gas flow rate [25], the inlet and outlet pressure, and the column temperature [22]. GC2014 is fully automated and equipped with flow rate fluctuation correction controlled by the GC software. Data handling and analysis of chromatographic data were made possible by special home-customized programs which were created to enable the variety of thermodynamic calculations used by the IGC method. To eliminate the contribution of the “inert” solid support to the retention volume, measurements of all 27 solutes were made using a blank chromatographic column packed with only the solid support (0% loading). The retention time of each solute was subtracted from the net retention volume illustrated in Eqn. (A4). The retention volumes of solutes on a zero loading column (support only) were interpolated over a wide range of temperatures, then subtracted from those measured on loaded columns. This automated system was fast and ideal for routine IGC measurements.

Vanishingly small amounts (0.10 µL) of selected solutes were injected into the chromatographic column. This small volume was tested to yield an absolute value of the solutes’ retention volumes. Chromatographic columns were made in the laboratory from 5-ft-long copper tubing, 1/4 inch in o.d. All copper columns were washed with methanol and annealed for several hours before use. Five chromatographic columns were prepared from five solutions containing different weight fractions of the blend (two columns of pure AP and PHBA and 3 columns of three different weight fraction blends). Each solution was prepared by dissolving a certain amount of AP, PHBA, and three blends in the appropriate solvent and deposited onto 7.921 g Chromosorb W using a soaking method developed by us earlier [22]. The resulting load of the AP-PHBA on the column was maintained at around 6.30-7.00% to ensure column porosity and to prevent any kinetic effects. Full descriptions of these columns are illustrated in Table 1. All columns were studied under identical conditions of temperature, flow rate, and inlet and outlet pressure of the carrier gas. Experiments were performed with 10 °C increments starting at 80 °C. The GC oven was operated continuously, and the columns’ temperature was increased by increments of 10 degrees to eliminate the possibility of recrystallization of the polymers, should the column cool before the study is complete.

**Table 1.** Chromatographic column description.

| Type | Wt. of AP | Wt. of PHBA | Volume fraction AP | Volume fraction PHBA | Solvent | Wt. of support | % Loading |
|---|---|---|---|---|---|---|---|
| 100% AP | 0.4935 g | 0.00 g | 1.00 | 0.00 | Methanol | 7.921 g | 6.24% |
| 100% PHBA | 0.00 g | 0.4900 g | 0.00 | 1.00 | Chloroform | 7.890 g | 6.28% |
| 25-75% AP- PHBA | 0.1260 g | 0.3740 g | 0.2520 | 0.7748 | Chloroform + Acetonitrile | 7.890 g | 6.31% |
| 50-50% AP- PHBA | 0.2532 g | 0.2532 g | 0.5064 | 0.4936 | Chloroform + Acetonitrile | 7.890 g | 6.39% |
| 75-25% AP- PHBA | 0.3760 g | 0.1240 g | 0.2752 | 0.2480 | Chloroform + Acetonitrile | 7.890 g | 6.33% |

## 4. RESULTS AND DISCUSSION

### 4.1. Thermal analysis

Amylopectin (AP) with a molar mass of 6 x $10^6$ gram/mol was thermally characterized by the melting point determination using Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) methods. AP decomposed at approximately 343 °C with an approximate 80% weight loss. The polymer showed two transitions at approximately 105 °C (identified as a $T_g$) accompanied by a 6% weight loss and at approximately 166 °C with no measurable weight loss. The melting point of AP was determined by the supplier as 174 °C and confirmed by the IGC [26]. The molar mass of the PHBA was determined by Gel Permeation Chromatography (GPC) which confirmed PHBA's polydispersity. PHBA has a weight average of $M_w^- = 65676$ g/mol, a number average of $M_n^- = 39016$ g/mol and polydispersity of 1.68. Its $T_g$ and $T_m$ were determined by DSC as 18 and 174 °C, respectively. The thermal degradation occurred around 250 °C as determined by Shimadzu's TGA 50.

### 4.2. Retention diagrams and molar heat of sorption

Recently, we reported the morphology changes and the thermal analysis of pure AP using DSC and TGA methods [26]. IGC complemented the DSC and TGA findings by identifying the glass transition and melting temperatures. Our findings showed that IGC is capable (as the DSC method) of analyzing the morphology of a polymeric system as a function of temperature. From the experimental chromatographic quantities, retention diagrams (thermal isotherms) of pure AP, pure PHBA and their blends were generated. According to Eqn. (A10), a plot of ln $V_g^o$ of each solute series versus 1/T was generated to be used as the retention diagram of that series. If the polymer and its blends are semicrystalline as in the case of AP and PHBA blends, the isotherms are expected to show several thermal changes due to the change in the morphology as temperature increases. However, PHBA has a $T_g$ around 18 °C, and it is considered to be amorphous above 80 °C; therefore, pure PHBA's retention diagrams were found to be generally linear and no thermal changes were found [27]. Thus, retention diagrams of AP and PHBA blends are expected to show at least two zones due to crystallinity of AP: crystalline and amorphous zones. The detection of these zones will show the change in the melting temperatures ($T_m$) of AP as it is blended with PHBA. However, the detection of these temperatures depends on the weight fraction of AP in the blend, which is capable of influencing the morphology of the blends. We recently reported the IGC retention diagrams of AP which showed its $T_g$ (105 °C) and $T_m$ (174 °C) [26].

Since both AP and PHBA decompose above 200 °C, experiments were not conducted above 170 °C. The retention diagrams of pure AP [26] and PHBA [27] have been published earlier. AP showed a change in the thermal isotherm clearly indicating its $T_g$ and $T_m$ temperatures. However, PHBA did not show any changes due to its $T_g$ being lower than the experimental range of 80-170 °C. When PHBA is blended with semi-crystalline AP in three different compositions, the morphology of the resulting blends has a mixture of amorphous and crystalline regions. Since a large number of retention diagrams were generated, representatives of retention diagrams of families with larger number of solutes (alkanes and halogenated families) were selected for the purpose of publication, Figures B1-B6 in Appendix B. $T_m$ of AP is expected to be lowered because of the blending of AP and PHBA at different weight fractions, a phenomenon called melting point depression. However, the alkane series did not show a clear change in the isotherm at all weight fractions used (Figures B1, B3 and B5) due to the limited specific interactions with the blend. In contrast, the halogenated family which exhibited a stronger specific interaction with the blends showed curvatures in the isotherm (Figures B2, B4 and B6). The position of the curvatures is dependent on the weight fraction of the blend. Thus, the blends' $T_m$ can be measured from the retention diagrams of all families (Table 2). All families agreed on $T_m$ within the experimental error; the average was calculated which clearly shows that the $T_m$ increases with the decrease in PHBA weight fraction.

The linear portion of all retention diagrams is an indication that the homopolymers and their blends are at an amorphous state at the experiments' temperature. Therefore, the thermodynamics are amenable for interpretation at this zone due to the establishment of the equilibrium between the polymeric stationary phase and the mobile phase (solutes' vapor). According to Eqn. (A10), the slope of the straight lines of all solutes' retention volumes represents the molar heat of sorption, $\Delta H_s^1$, of solutes' vapor into the surface of the polymer. Since the chemical nature of solutes are different among and within the families, it is expected that the values of $\Delta H_s^1$ differ from one solute to another within the family and from one family to another depending on the affinity of the solutes to the AP, PHBA and blends. $\Delta H_s^1$ values of all solutes and all columns ranging from -19.41 KJ/mol of acetone to -90.38 KJ/mol of cyclohexane are shown in Table 3. These values reflect the strength and types of interactions of the solutes with the polymeric surface of all columns. Cyclohexane has much less affinity to all the columns than acetone. Inspection of alkanes' $\Delta H_s^1$ values reveals an interesting systematic increase as a $CH_2$ group is added to the backbone of the alkane family. A plot of $\Delta H_s^1$ versus number of $CH_2$ groups in the alkane's family showed a contribution of -5.41 KJ/mol for each $CH_2$ group added to the backbone of the alkane family [27]. As AP is blended with PHBA, $\Delta H_s^1$ values of alkanes and six-membered rings (representing dispersive forces) showed a decrease (more endothermic) because the weight fraction of AP decreases in the blend. However, acetates (representing dispersive and dipole-dipole) did not show a clear change in values as in the case of alkanes. Ether and ketones showed an increase in values (more exothermic) as AP weight fraction decreased due to the increased affinity of these solutes (which can be considered as a proton donor) to the exposed portion of PHBA which has

**Table 2.** Melting temperatures of pure AP, pure PHBA and three compositions of AP-PHBA blends as determined by IGC.

| Solutes | 100% AP °C | AP 75% - PHBA 25% °C | AP 50% - PHBA 50% °C | AP 25% - PHBA 75% °C | 100% PHBA* °C |
|---|---|---|---|---|---|
| **Alkanes** | 171 | --- | 90.50 | 87.90 | 174 |
| **Acetates** | 174 | 97.2 | 90.50 | 87.90 | 174 |
| **Halogenated** | 162 | 94.50 | 90.50 | 86.60 | 174 |
| **Ether and ketones** | 162 | 90.50 | 90.5 | 89.20 | 174 |
| **6-membered rings** | --- | 90.50 | 86.60 | 89.20 | 174 |
| **Average** | 167.25 | 94.10 | 88.53 | 87.90 | 174 |

*Pure PHBA melting point was determined by DSC and confirmed by the supplier.

**Table 3.** The molar heat of sorption, $\Delta H_s^1$, of 100% PHBA and three compositions of its blends (KJ/mol).

| **Alkanes** | **100% PHB** | **25% PHBA-75% AP** | **50% PHBA-50% AP** | **75% PHBA-25% AP** |
|---|---|---|---|---|
| Hexane | -30.2962 | -23.3623 | -25.9397 | -22.8635 |
| Heptane | -30.5298 | -36.0828 | -27.1036 | -23.2792 |
| Octane | -38.2777 | -33.6717 | -28.3507 | -21.1176 |
| Nonane | -44.7376 | -44.7293 | -40.3229 | -26.2722 |
| Decane | -51.2616 | -45.0619 | -47.5561 | -33.838 |
| Undecane | -55.5109 | -47.9718 | -48.72 | -39.5746 |
| Dodecane | -59.8176 | -53.2096 | -55.5375 | -37.1636 |
| **Acetates** | | | | |
| Methyl acetate | -29.6535 | -26.6048 | -28.6833 | -38.6601 |
| Ethyl acetate | -45.3471 | -32.5909 | -36.1659 | -27.0205 |
| Propyl acetate | -37.0331 | -31.4269 | -41.4037 | -30.1798 |
| n-Butyl acetate | -47.6376 | -26.106 | -44.8956 | -35.1682 |
| **Ether and ketones** | | | | |
| Tetrahydrofuran | -25.5498 | -18.6234 | -31.0112 | -39.0758 |
| Dioxin | -38.6194 | -40.7386 | -32.092 | -37.995 |
| Acetone | -19.4065 | -31.3438 | -22.2815 | -26.6879 |
| Methyl ethyl ketone | -31.1634 | -29.3484 | -35.5008 | -34.8357 |
| **Halogenated** | | | | |
| Methylene chloride | -25.7127 | -21.949 | -22.7804 | -32.5909 |
| 1,2-Dichloroethane | -38.424 | -23.0298 | -38.577 | -31.9258 |
| Chloroform | -31.4261 | -16.9606 | -35.1682 | -35.2514 |
| Chlorobenzene | -45.2897 | -31.8426 | -38.3275 | -38.4107 |
| Pentyl chloride | -36.8917 | -28.6833 | -34.6694 | -24.6926 |
| Trichloro ethylene | -32.906 | -25.1083 | -34.0874 | -39.5746 |
| Methyl chloroform | -45.2897 | -31.8426 | -40.406 | -41.57 |
| Carbon tetrachloride | -30.465 | -24.6094 | -32.0089 | -32.7572 |
| Butyl chloride | -33.0947 | -30.8449 | -34.0874 | -32.092 |
| **Six-membered ring** | | | | |
| Cyclohexane | -90.3815 | -28.7664 | -39.0758 | -19.621 |
| Cyclohexene | -24.3326 | -21.8658 | -36.5816 | -15.6303 |
| Toluene | -34.7683 | -34.6694 | -26.8542 | -35.9165 |

carbonyl groups as proton acceptors along the main chain. The halogenated group showed mixed results depending on the specific interaction that each solute provided.

### 4.3. Interaction parameters $\chi_{12}$, $\chi_{13}$, $\chi_{1\text{-blend}}$ and $\chi_{23}'$

In this section the strength of solute's interactions with pure AP, pure PHBA and blends will be explored; they are designated as $\chi_{12}$, $\chi_{13}$ and $\chi_{1\text{-blend}}$. The strength of interactions among the polymer pair (AP-PHBA) will also be explored; it is designated as $\chi_{23}'$. The interaction parameters, $\chi_{12}$, for solutes-pure AP and $\chi_{13}$, for solutes-pure PHBA were reported earlier [27]. These interaction parameters will be used in the calculations of $\chi_{23}'$ in the next sections. Since the $T_m$ of the three blends dropped below 100 °C, the calculations of all interaction parameters will be performed from 100 to 120 °C which is well above the blends' $T_g$. This is to ensure that the equilibrium between the mobile and the stationary phases is established and there is no kinetic effect due to crystallinity; thus, the thermodynamic calculations are valid for interpretation.

### 4.4. Solutes-blends' interaction parameters, $\chi_{1\text{-blend}}$

$\chi_{1\text{-blend}}$ for the interaction of solutes with three weight fractions of AP-PHBA blends were calculated according to Eqn. (A11). If these interactions are strong, the blends and the solute are compatible (soluble) with each other; thus, negative $\chi_{1\text{-blend}}$ values (exothermic) are expected. If the interactions are weak, $\chi_{1\text{-blend}}$ values are expected to be positive (endothermic) and a separation of the components will occur. Tables 4-6 show the values of $\chi_{1\text{-blend}}$ of three weight fractions of AP-PHBA blends in thetemperature range of 80-150 °C. The three compositions showed positive values of $\chi_{1\text{-blend}}$ decreasing slightly with increasing temperatures.

**Table 4.** Interaction parameter ($\chi_{1\text{-blend}}$) of solute-75% AP & 25% PHBA system (120 °C -150 °C).

| **Alkanes** | **120 °C** | **130 °C** | **140 °C** | **150 °C** | **Av. $\chi'_{1\text{-blend}}$** |
|---|---|---|---|---|---|
| Hexane | 2.35 | 1.93 | 1.42 | 2.69 | 0.015 |
| Heptane | 2.33 | 2.53 | 3.05 | 1.94 | 0.015 |
| Octane | 2.71 | 2.93 | 4.14 | 2.73 | 0.015 |
| Nonane | 3.00 | 3.20 | 3.48 | 3.49 | 0.015 |
| Decane | 3.24 | 3.36 | 3.60 | 2.97 | 0.015 |
| Undecane | 3.30 | 3.33 | 3.34 | 3.68 | 0.015 |
| Dodecane | 3.31 | 3.27 | 3.36 | 3.68 | 0.014 |
| **Acetates** | | | | | |
| Methyl acetate | 1.10 | --- | --- | --- | 0.018 |
| Ethyl acetate | 2.05 | --- | --- | --- | 0.015 |
| Propyl acetate | 2.10 | 1.95 | --- | --- | 0.016 |
| n-Butyl acetate | 2.12 | 2.14 | 2.00 | 2.26 | 0.015 |
| **Ether and ketones** | | | | | |
| Tetrahydrofuran | 1.76 | --- | --- | --- | 0.017 |
| Dioxin | 1.95 | 2.00 | --- | --- | 0.020 |
| Acetone | 1.27 | --- | --- | --- | 0.020 |
| Methyl ethyl ketone | 2.30 | --- | --- | --- | 0.017 |
| **Halogenated** | | | | | |
| Methylene chloride | 2.23 | --- | --- | --- | 0.021 |
| 1,2-dichloroethane | 1.01 | 0.98 | 0.69 | 0.62 | 0.021 |
| Chloroform | 2.24 | 1.50 | 2.13 | 2.17 | 0.022 |
| Chlorobenzene | 2.61 | 2.67 | 2.57 | 2.90 | 0.021 |
| Butyl chloride | 1.72 | --- | --- | --- | 0.014 |
| Pentyl chloride | 2.34 | 2.66 | 2.34 | --- | 0.016 |
| Trichloro ethylene | 2.71 | 2.48 | 2.57 | 2.45 | 0.021 |
| Methyl chloroform | 0.98 | 1.24 | --- | --- | 0.005 |
| Carbon tetrachloride | 2.65 | 2.86 | 2.22 | 2.14 | 0.023 |
| **Six-membered ring** | | | | | |
| Cyclohexane | 2.19 | 2.80 | 2.09 | --- | 0.015 |
| Cyclohexene | 2.45 | 3.06 | 2.38 | 1.85 | 0.014 |
| Toluene | 2.52 | 2.81 | 1.93 | 2.70 | 0.021 |

Note: Dashed lines indicate that experiments were not performed or Antoine Constants are not available for calculation.

**Table 5.** Interaction parameter ($\chi_{1\text{-blend}}$) of solute-50% AP - 50% PHBA system (120 °C -150 °C).

| **Alkanes** | **120 °C** | **130 °C** | **140 °C** | **150 °C** | **Average $\chi'_{1\text{-blend}}$** |
|---|---|---|---|---|---|
| Hexane | 2.89 | 3.29 | 2.15 | 2.15 | 0.016 |
| Heptane | 2.45 | 2.32 | 1.67 | 1.67 | 0.013 |
| Octane | 3.18 | 2.80 | 2.15 | 2.15 | 0.014 |
| Nonane | 2.96 | 3.45 | 2.63 | 2.63 | 0.013 |
| Decane | 3.10 | 3.30 | 3.25 | 3.25 | 0.012 |
| Undecane | 3.36 | 3.40 | 3.28 | 3.28 | 0.012 |
| Dodecane | 3.47 | 3.54 | 3.47 | 3.47 | 0.012 |
| **Acetates** | | | | | |
| Methyl acetate | 1.65 | --- | --- | --- | 0.012 |
| Ethyl acetate | 1.83 | --- | --- | --- | 0.016 |
| Propyl acetate | 2.25 | 2.34 | --- | --- | 0.017 |
| n-Butyl acetate | 2.26 | 2.57 | 2.44 | 2.04 | 0.012 |
| **Ether and ketones** | | | | | |
| Tetrahydrofuran | 1.99 | --- | --- | --- | 0.020 |
| Dioxin | 1.93 | --- | --- | --- | 0.020 |
| Acetone | 1.61 | --- | --- | --- | 0.020 |
| Methyl ethyl ketone | 2.06 | --- | --- | --- | 0.020 |
| **Halogenated** | | | | | |
| Methylene chloride | 1.98 | --- | --- | --- | 0.020 |
| 1,2-dichloroethane | 1.52 | 1.55 | 1.29 | 1.29 | 0.015 |
| Chloroform | 1.87 | 2.22 | 2.13 | 2.13 | 0.020 |
| Chlorobenzene | 2.36 | 2.59 | 2.05 | 2.05 | 0.020 |
| Butyl chloride | 2.37 | --- | --- | --- | 0.020 |
| Pentyl chloride | 2.47 | 2.67 | --- | --- | 0.020 |
| Trichloro ethylene | 2.17 | 2.55 | 2.40 | 2.40 | 0.020 |
| Methyl chloroform | 0.72 | 0.96 | --- | --- | 0.010 |
| Carbon tetrachloride | 2.47 | 2.77 | 2.59 | 2.18 | 0.020 |
| **Six-membered ring** | | | | | |
| Cyclohexane | 2.27 | 2.83 | 2.55 | --- | 0.020 |
| Cyclohexene | 2.06 | 2.80 | 3.16 | 2.50 | 0.020 |
| Toluene | 2.42 | 2.72 | 2.47 | 1.81 | 0.015 |

Note: Dashed lines indicate that experiments were not performed or Antoine Constants are not available for calculation.

**Table 6.** Interaction parameter ($\chi_{1\text{-blend}}$) of solute-25%AP-75 %PHBA systems (120-150 °C).

| **Alkanes** | **120 °C** | **130 °C** | **140 °C** | **150 °C** | **Average $\chi'_{1\text{-blend}}$** |
|---|---|---|---|---|---|
| Hexane | 1.82 | 2.01 | 1.92 | 1.31 | 0.010 |
| Heptane | 2.20 | 2.01 | 3.26 | 1.84 | 0.013 |
| Octane | 2.61 | 2.45 | 2.77 | 2.29 | 0.013 |
| Nonane | 2.96 | 2.83 | 2.68 | 2.64 | 0.013 |
| Decane | 3.27 | 3.14 | 2.90 | 3.00 | 0.013 |
| Undecane | 3.61 | 3.41 | 3.34 | 3.22 | 0.014 |
| Dodecane | 3.68 | 3.63 | 3.67 | 3.52 | 0.014 |
| **Acetates** | | | | | |
| Methyl acetate | 1.56 | --- | --- | --- | 0.014 |
| Ethyl acetate | 1.82 | --- | --- | --- | 0.014 |
| Propyl acetate | 2.02 | 2.27 | --- | --- | 0.014 |
| n-Butyl acetate | 2.02 | 2.58 | 1.85 | 1.81 | 0.013 |
| **Ether and ketones group** | | | | | |
| Tetrahydrofuran | 1.91 | --- | --- | --- | 0.020 |
| Dioxin | 1.83 | 1.69 | --- | --- | 0.020 |
| Acetone | 1.65 | --- | --- | --- | 0.020 |
| Methyl ethyl ketone | 1.64 | --- | --- | --- | 0.016 |
| **Halogenated** | | | | | |
| Methylene chloride | 1.65 | --- | --- | --- | 0.020 |
| 1,2-dichloroethane | 1.26 | 1.83 | 1.49 | 1.86 | 0.019 |
| Chloroform | 1.93 | 1.97 | 1.55 | 2.18 | 0.020 |
| Chlorobenzene | 2.24 | 2.45 | 2.45 | 2.21 | 0.019 |
| Butyl chloride | 1.92 | --- | --- | --- | 0.016 |
| Pentyl chloride | 2.21 | 2.06 | 1.95 | --- | 0.015 |
| Trichloro ethylene | 1.96 | 2.55 | 2.08 | 2.26 | 0.021 |
| Methyl chloroform | 0.58 | 0.64 | --- | --- | 0.005 |
| Carbon tetrachloride | 2.10 | 3.36 | 2.35 | 2.07 | 0.015 |
| **Six-membered ring** | | | | | |
| Cyclohexane | 1.98 | 1.84 | 1.73 | --- | 0.015 |
| Cyclohexene | 2.12 | 2.48 | 1.6 | --- | 0.016 |
| Toluene | 2.09 | 2.73 | 2.62 | --- | 0.018 |

Note: Dashed lines indicate that experiments were not performed or Antoine Constants are not available for calculation.

The chemical nature of the families' effect on $\chi_{1\text{-blend}}$ is well pronounced. Considering the high molar mass and the complexity of the AP (proton donor) structure, the strength of the specific interactions of its blends with PHBA (proton acceptor) were consistent among the solutes. The whole system is considered to be more complex than a ternary system; one would expect a variation in $\chi_{1\text{-blend}}$ values due to the chemical nature of the solutes and the types of the specific forces involved.

Recently, we looked into this effect which has been a dilemma for IGC researchers for quite some time. We pointed out in our previous publications [22], that $\chi$ values, in general, depended on the chemical nature of the solute, and concluded that this effect is not due to IGC fault, but due to the limitation of the Flory-Huggins Theory. The theory assumes that Gibbs' free energy of mixing is additive with respect to the binary contributions. Several IGC researchers debated this effect and attempted to find solutions by which the effect of the chemical nature of solutes on $\chi_{12}, \chi_{13}, \chi_{1\text{-}blend}$ and $\chi_{23}'$ can be eliminated [18, 26, 27]. Much of the discussion was centered on the role of several types of interactions, such as dispersive forces, dipole-dipole and H-bonding, in determining $\chi$ parameter. Also, another factor caused $\chi$ values to depend on the chemical nature of solute because of the non-randomness of the mobile phase partitioning its molecules between the surface layer of the stationary phase.

In an attempt to eliminate the solutes' chemical nature dependency, we corrected the values $\chi_{\text{l-blend}}$ using the molar volume ($V_1$) of each solute at the experiments' temperature as follows:

$$\chi'_{l-blend} = \frac{\chi_{l-blend}}{V_1} \tag{4}$$

Molar volume, $V_1$, of all solutes were calculated using Antoine Constants found in the literature [19, 22]. The new term, $\chi'_{\text{l-blend}}$ is a corrected form of $\chi_{\text{l-blend}}$ free from the dependence of the chemical nature of solutes. Accordingly, all values of $\chi'_{\text{l-blend}}$ (Tables (4-6)) became zero after the correction procedure, which is an indication of a moderate affinity of all solutes to AP-PHBA blends. $\chi'_{\text{l-blend}}$ values fluctuated only slightly; however, all solutes agreed well within experimental error, showing no dependence on the chemical nature of solutes. The last column in Tables (4-6) shows the average $\chi'_{\text{l-blend}}$ values of each solute calculated at each temperature. The corrected values of $\chi'_{\text{l-blend}}$ indicate modest exothermicity of interactions of all solutes with the three blends. It is surprising, however, that the exothermicity is not as strong as anticipated.

### 4.5. Polymer-polymer interaction parameters, $\chi_{23}'$

To evaluate the strength of the specific interactions (compatibility or solubility) between the polymer pair, the polymer-polymer interaction parameter, $\chi_{23}'$ (Eqn. A15) has to be calculated. AP has a large molar mass and its backbone is covered with hydroxyl functional groups which are proton donor groups. On the other hand, PHBA, both the acid and the ester forms, has a much smaller molar mass as compared to that of AP. PHBA backbone has carbonyl groups as proton acceptors along the main chain. One would expect H-bonding interactions to develop between the two polymers. Thus, exothermic values for $\chi_{23}'$ are expected; however, the magnitude of the strength of these interactions is in question and will be discussed in this section. Tables 7-9 show $\chi_{23}'$ for the three weight fractions of AP-PHBA blends at a temperature range of 100-120 °C. These tables show exothermic values of $\chi_{23}'$ for all three weight fractions at the range of temperature used. The compatibility of the polymer pair using all solutes was found to be coherent and the interactions between the polymer pair were moderate in strength.

Generally speaking, there is no evidence of separation of the polymer pair at all temperatures and weight fractions used. However, as mentioned in the previous section, the degree of compatibility of the polymer-pair differed from one family to another and among the solutes within the family itself. The values of $\chi_{23}'$ differ from one family to another due to the chemical nature and the type of interaction forces involved, as was first pointed out by us in earlier publications [13-14, 19, 22]. The values ranged between zero and -5.50 at the temperature range used. Since the surface concentration of one polymer in the blend always exceeded the bulk composition (wt% ratio), the differences in these two parameters varied strongly with the choice of the vapor solute used. Another factor that contributes to these differences is the preferential adsorption of the host polymer (AP) on the chromatographic support and the migration of the diluent polymer (PHBA) to the surface of the stationary phase.

Similar to our corrections in Eqn. (4), the values of $\chi_{23}'$ were corrected for the effect of the chemical nature of solutes expressed in the molar volume of solutes ($V_1$):

$$\chi_{23}^{-} = \frac{\chi_{23}'}{V_1} \tag{5}$$

$\chi^{-}_{23}$ represents the polymer-polymer interaction that is independent of the chemical nature of solutes. Tables 7-9 show that the corrected values

**Table 7.** Interaction parameters ($\chi_{23}$ and $\bar{\chi}_{23}$) of solutes, 75% AP - 25% PHBA system (100-120 °C).

| **Temperature** | **100 °C** | | **110 °C** | | **120 °C** | |
|---|---|---|---|---|---|---|
| **Alkanes** | $\chi_{23}$ | $\bar{\chi}_{23}$ | $\chi_{23}$ | $\bar{\chi}_{23}$ | $\chi_{23}$ | $\bar{\chi}_{23}$ |
| Hexane | -5.57 | -0.034 | --- | --- | -1.56 | -0.010 |
| Heptane | -3.93 | -0.024 | -6.04 | -0.000 | -3.37 | -0.020 |
| Octane | -0.98 | -0.005 | -5.46 | -0.033 | -4.92 | -0.027 |
| Nonane | -1.98 | -0.010 | -2.61 | -0.028 | -4.99 | -0.025 |
| Decane | -4.01 | -0.019 | -4.08 | -0.012 | -5.07 | -0.023 |
| Undecane | -4.34 | -0.019 | -4.14 | -0.018 | -4.72 | -0.020 |
| Dodecane | -4.13 | -0.017 | -7.33 | -0.017 | -4.30 | -0.017 |
| **Acetates** | | | | | | |
| Methyl acetate | -0.33 | -0.004 | -0.86 | -0.001 | --- | --- |
| Ethyl acetate | -1.63 | -0.015 | -0.91 | -0.091 | -1.21 | -0.010 |
| Propyl acetate | -0.23 | -0.002 | -0.76 | -0.075 | -4.33 | -0.033 |
| n-Butyl acetate | -0.63 | -0.004 | -2.76 | -0.019 | -1.14 | -0.015 |
| **Ether and ketones** | | | | | | |
| Tetrahydrofuran | -1.16 | -0.033 | -1.41 | -0.015 | -4.50 | -0.046 |
| Dioxin | -2.97 | -0.024 | --- | --- | -0.76 | -0.008 |
| Acetone | -1.95 | -0.006 | -2.76 | -0.033 | -2.11 | -0.024 |
| Methyl ethyl ketone | -0.64 | -0.006 | -2.83 | -0.028 | -5.34 | -0.052 |
| **Halogenated** | | | | | | |
| Methylene chloride | -1.11 | -0.024 | -3.42 | -0.039 | -3.71 | -0.041 |
| 1,2-Dichloroethane | -0.98 | -0.014 | -4.10 | -0.060 | -2.65 | -0.035 |
| Chloroform | -1.00 | -0.011 | -5.36 | -0.064 | -4.46 | -0.052 |
| Chlorobenzene | -1.24 | -0.011 | -0.33 | -0.035 | -1.81 | -0.046 |
| Butyl chloride | -0.64 | -0.005 | --- | --- | -2.31 | -0.020 |
| Pentyl chloride | -1.11 | -0.008 | --- | --- | -3.08 | -0.020 |
| Trichloro ethylene | -1.68 | -0.017 | -7.16 | -0.035 | -6.14 | -0.052 |
| Methyl chloroform | --- | --- | --- | --- | --- | --- |
| Carbon tetrachloride | --- | --- | -7.16 | -0.066 | -6.35 | -0.057 |
| **Six-membered ring** | | | | | | |
| Cyclohexene | -0.64 | -0.008 | -5.49 | -0.050 | -4.69 | -0.040 |
| Benzene | -0.25 | -0.002 | -7.33 | -0.060 | -5.62 | -0.050 |
| Toluene | -1.82 | -0.027 | -1.56 | -0.013 | -3.44 | -0.029 |

Note: Dashed lines indicate that experiments were not performed or Antoine Constants are not available for calculation.

**Table 8.** Interaction parameters ($\chi'_{23}$ and $\bar{\chi}_{blend}$) of solutes, 50% AP - 50% PHBA system (100 °C - 120 °C).

| **Temperature** | **100 °C** | | **110 °C** | | **120 °C** | |
|---|---|---|---|---|---|---|
| **Alkanes** | $\chi'_{23}$ | $\bar{\chi}_{23}$ | $\chi'_{23}$ | $\bar{\chi}_{23}$ | $\chi'_{23}$ | $\bar{\chi}_{23}$ |
| Hexane | -4.75 | -0.032 | -3.00 | -0.02 | -2.95 | -0.019 |
| Heptane | -4.91 | -0.030 | -5.38 | -0.018 | -3.68 | -0.020 |
| Octane | -4.59 | -0.026 | -3.37 | -0.030 | -5.88 | -0.032 |
| Nonane | -2.70 | -0.014 | -2.74 | -0.017 | -4.00 | -0.020 |
| Decane | -4.30 | -0.029 | -3.87 | -0.013 | -3.48 | -0.016 |
| Undecane | -4.15 | -0.018 | -4.03 | -0.017 | -4.12 | -0.018 |
| Dodecane | -4.01 | -0.016 | -8.70 | -0.016 | -4.11 | -0.016 |
| **Acetates** | | | | | | |
| Methyl acetate | -3.10 | -0.035 | -1.86 | -0.020 | --- | --- |
| Ethyl acetate | -2.15 | -0.020 | -2.12 | -0.020 | 0.00 | 0.000 |
| Propyl acetate | -3.15 | -0.025 | -1.96 | -0.015 | -4.54 | -0.034 |
| n-Butyl acetate | -1.11 | -0.007 | -3.08 | -0.021 | -1.55 | -0.010 |
| **Ether and ketones** | | | | | | |
| Tetrahydrofuran | -2.43 | -0.026 | -4.66 | -0.050 | -5.02 | -0.05 |
| Dioxin | -1.06 | -0.011 | --- | --- | -1.51 | -0.016 |
| Acetone | -1.64 | -0.020 | -3.21 | -0.040 | -2.91 | -0.034 |
| Methyl ethyl ketone | -1.49 | -0.015 | -2.34 | -0.023 | -3.50 | -0.034 |
| **Halogenated** | | | | | | |
| Methylene chloride | -0.97 | -0.11 | -3.27 | -0.037 | -2.34 | -0.026 |
| 1,2-dichloroethane | -1.06 | -0.022 | -4.80 | -0.065 | -3.98 | -0.05 |
| Chloroform | -1.36 | -0.016 | -3.73 | -0.040 | -4.51 | -0.053 |
| Chlorobenzene | -0.90 | -0.008 | -1.30 | -0.012 | -2.13 | -0.019 |
| Butyl chloride | -1.19 | -0.010 | --- | --- | -4.83 | -0.040 |
| Pentyl chloride | -1.64 | -0.012 | --- | --- | -3.01 | -0.028 |
| Trichloro ethylene | -0.20 | -0.002 | -3.93 | -0.040 | -3.23 | -0.031 |
| Methyl chloroform | --- | --- | --- | --- | --- | --- |
| Carbon tetrachloride | --- | --- | --- | --- | -4.49 | -0.040 |
| **Six-membered ring** | | | | | | |
| Cyclohexene | -0.64 | -0.006 | -5.11 | -0.044 | -4.58 | -0.040 |
| Benzene | -0.62 | -0.005 | -8.69 | -0.070 | -3.24 | -0.026 |
| Toluene | -1.82 | -0.016 | -3.55 | -0.030 | -3.40 | -0.028 |

Note: Dashed lines indicate that experiments were not performed or Antoine constants are not available for calculation.

of $\bar{\chi}_{23}$ for the three blends' compositions hovered around the -0.0 mark for all solutes, an indication of modest interaction between the polymer pair. These values fluctuated slightly, within the experimental error. There is no indication of which weight fraction favors the miscibility of one polymer pair over the other.

The modest compatibility of AP and PHBA is a surprise, since both have proton donor-acceptor functional groups. The literature showed similar

**Table 9.** Interaction parameters ($\chi'_{23}$ and $\bar{\chi}_{23}$) of solute-25% AP & 75% PHBA system (100 °C - 120 °C).

| **Temperature** | **100 °C** | | **110 °C** | | **120 °C** | |
|---|---|---|---|---|---|---|
| **Alkanes** | $\chi'_{23}$ | $\bar{\chi}_{23}$ | $\chi'_{23}$ | $\bar{\chi}_{23}$ | $\chi'_{23}$ | $\bar{\chi}_{23}$ |
| Hexane | -0.06 | -0.000 | --- | --- | -0.68 | -0.004 |
| Heptane | -2.51 | -0.015 | -2.24 | -0.014 | -3.11 | -0.019 |
| Octane | -4.25 | -0.024 | -5.66 | -0.031 | -3.93 | -0.021 |
| Nonane | -5.43 | -0.028 | -3.67 | -0.019 | -4.64 | -0.023 |
| Decane | -6.12 | -0.029 | -6.51 | -0.030 | -4.48 | -0.021 |
| Undecane | -6.40 | -0.028 | --- | --- | -6.13 | -0.026 |
| Dodecane | -6.94 | -0.028 | --- | --- | --- | --- |
| **Acetates** | | | | | | |
| Methyl acetate | -1.16 | -0.013 | -2.01 | -0.022 | --- | --- |
| Ethyl acetate | -1.14 | -0.010 | -1.19 | -0.011 | -0.64 | -0.006 |
| Propyl acetate | -2.97 | -0.023 | -1.69 | -0.013 | -3.53 | -0.027 |
| n-Butyl acetate | -3.55 | -0.024 | -5.08 | -0.035 | -1.84 | -0.012 |
| **Ether and ketones** | | | | | | |
| Tetrahydrofuran | -0.72 | -0.008 | -1.17 | -0.012 | -6.00 | -0.062 |
| Dioxin | -2.13 | -0.024 | --- | --- | -1.44 | -0.016 |
| Acetone | -0.68 | -0.008 | -3.79 | -0.045 | -2.66 | -0.031 |
| Methyl ethyl ketone | -0.80 | -0.008 | -3.64 | -0.036 | -1.54 | -0.015 |
| **Halogenated** | | | | | | |
| Methylene chloride | -1.83 | -0.021 | -4.04 | -0.046 | -0.66 | -0.007 |
| 1,2-dichloroethane | -2.64 | -0.036 | -3.67 | -0.050 | -2.56 | -0.033 |
| Chloroform | -2.56 | -0.031 | -3.44 | -0.041 | -6.98 | -0.082 |
| Chlorobenzene | -2.43 | -0.022 | -3.72 | -0.033 | -3.17 | -0.062 |
| Butyl chloride | -3.20 | -0.031 | --- | --- | -3.43 | -0.029 |
| Pentyl chloride | -2.1 | -0.016 | --- | --- | -3.74 | -0.027 |
| Trichloro ethylene | -2.12 | -0.021 | -3.82 | -0.038 | -2.84 | -0.028 |
| Methyl chloroform | --- | --- | --- | --- | --- | --- |
| Carbon tetrachloride | -2.29 | -0.027 | -3.71 | -0.034 | -3.26 | -0.029 |
| **Six-membered ring** | | | | | | |
| Cyclohexane | -1.73 | -0.015 | -3.25 | -0.028 | -4.35 | -0.037 |
| Cyclohexene | -1.28 | -0.011 | -3.01 | -0.025 | -4.05 | -0.033 |
| Toluene | -2.36 | -0.020 | -2.74 | -0.023 | -2.99 | -0.025 |

Note: Dashed lines indicate that experiments were not performed or Antoine Constants are not available for calculation.

results when PHBA was blended with starch acetate (SA) and studied using DSC [9]. FTIR studies showed that the O-H stretching band of SA in the blend remained almost in the same region as compared to that of pure SA, and the absorption of carbonyl groups in PHBA in the blend is independent of SA content at 1724 $cm^{-1}$. The C=O stretching band of carbonyl groups of SA was also constant at 1748 $cm^{-1}$. This observation concluded that there were no specific interactions which occurred between the two components. SEM, FTIR and DSC studies concluded that PHBA-SA blends are immiscible. The size of the SA phase is larger in the 40-60% PHBA-SA blend than in 80-20% PHBA-SA blend. Similar studies were conducted by blending PHBA with other biodegradable polymers such as poly (ethylene oxide), poly (vinyl alcohol) and poly (L-lactide) [28-33]. Some of the boxes in Tables 7-9 were left blank due to the absence of $\chi_{12}$, $\chi_{13}$, $\chi_{1\text{-blend}}$, and/or Antione constants in the literature at the temperature used in the experiment. These parameters have to be studied at identical experimental conditions in order for $\chi_{23}$' to be calculated (see 'Materials and Methods' section).

### 4.6. Crystallinity of AP-PHBA blends

IGC has been proven to be successful in calculating the degree of crystallinity of polymers, $\%X_c$ [1], in a more detailed way than other methods such as the DSC. From the chromatographic quantities outlined in Eqn. (A4), $V_g^o$ at two different zones can be measured: amorphous and crystalline [23]. The $\%X_c$ of AP as a semi-crystalline polymer was published by us [3] to be 85% at temperatures above 80 °C. PHBA has a $T_g$ below room temperature and it is in an amorphous state at our experimental range of temperatures. Using the retention volume diagrams of the blends, extrapolation of the linear portion of the amorphous region (above $T_m$) to the crystalline region will measure two retention volumes: $V_{g,sample}$, the retention volume of the solute in the crystalline region, and $V_{g,amorphous}$, the retention volume of the solute in the extrapolated amorphous region. Using the following relationship, the degree of the crystallinity can be assessed:

$$\%X_c = 100\{1-\{\frac{V_{g,sample}}{V_{g,amorphus}}\}\} \quad (6)$$

Using equation (6), the degree of crystallinity of the three weight fractions of the three blends was compared with that of the pure AP and PHBA. Table 10 shows that both AP and its blends are crystalline from 80 °C to 100 °C. AP, with a high molar mass, is considered as a host polymer and PHBA (lower molar mass) acts as a diluent polymer when it is blended. Therefore, blending AP with PHBA should show an effect on the $\%X_c$ of the blend. Indeed this is the case, and at 75% AP blend, a decrease in AP's $\%X_c$ occurred. The trend continued, and $\%X_c$ decreased even further as more PHBA was added and more dilution using PHBA occurred. $\%X_c$ significantly decreased with the rise in temperature as more crystals melted in the blend. Hence, a correlation between the degree of crystallinity and the compatibility of the blend can be drawn. These findings agree well with the melting points' depression data listed in Table 2.

### 4.7. Dispersive surface energy

Another test of the compatibility of the blend is to measure the dispersive component of the blends' surface energy, $\gamma^s_d$. This term only represents the dispersive component of surface energy when alkane series is used. The dispersive forces increase with the addition of more $CH_2$ groups to the alkanes' backbone. This does not represent the total surface energy of the blends as more contributions from other interaction forces such as acid-base to $\gamma^s_d$ can be utilized. IGC has been

**Table 10.** Degree of crystallinity of three compositions of AP-PHBA blends (80-100 °C).

| Temperature °C | 100% PHBA | 75-25% AP-PHBA | 50-50% AP-PHBA | 25-75% AP-PHBA | 100% AP* |
|---|---|---|---|---|---|
| 80 | 0 | 74.08 | 53.55 | 60.74 | 85-100 |
| 84 | 0 | 68.31 | 42.22 | 58.31 | 85-100 |
| 87 | 0 | 43.26 | 22.13 | 21.35 | 85-100 |
| 91 | 0 | 38.12 | 7.74 | 8.34 | 85-100 |
| 97 | 0 | 15.63 | 11.31 | 6.74 | 85-100 |
| 100 | 0 | 7.69 | 6.77 | 3.95 | 85-100 |

*Taken from our previous data (reference 1) for comparison.

**Table 11.** The dispersive surface energy of pure AP and 50% AP - 50% PHBA blends at 80-140 °C.

| **Temperature °C** | **$\gamma^s_d$ of 100% AP mJ/m$^2$** | **$\gamma^s_d$ mJ/m$^2$ 100% PHBA** | **$\gamma^s_d$ mJ/m$^2$ 75-25% AP-PHBA** | **$\gamma^s_d$ mJ/m$^2$ 50-50% AP-PHBA** | **$\gamma^s_d$ mJ/m$^2$ 25-75% AP-PHBA** |
|---|---|---|---|---|---|
| 80 | 25.35 | 24.42 | 25.08 | 22.94 | 15.22 |
| 90 | 23.56 | 24.12 | 21.75 | 28.33 | 21.31 |
| 100 | 21.79 | 25.20 | 20.04 | 23.75 | 10.97 |
| 110 | 19.23 | 19.38 | 34.56 | 21.93 | 9.27 |
| 120 | 17.06 | 13.94 | 14.93 | 22.25 | 6.59 |
| 130 | ---- | 22.80 | ---- | ---- | ---- |
| 140 | ---- | 19.43 | ---- | ---- | ---- |

successful in the calculation of the contribution of all attraction forces to $\gamma^s_d$; however, only the dispersive contribution is discussed in this paper. $\gamma^s_d$ of pure AP and pure HPBA were reported earlier by us [26, 27]. $\gamma^s_d$ of the blends' three compositions were calculated using only the alkane series in the temperature range of 80-120 °C. According to Eqn. (1), plots of RT ln $V_g^o$ in KJ/mol versus the number of carbons in the alkane series were generated for each temperature. Linear relationships were obtained and the slope of the straight lines was computed as the free energy of adsorption of a $CH_2$ group, $\Delta G_a^{CH2}$. Utilizing Eqn. (3), the dispersive component of the surface energy of AP-PHBA blends, $\gamma^s_d$, was calculated as a function of temperature. The cross-sectional area [34] of an adsorbed $CH_2$ group, $a_{CH2}$ is estimated to be 6 $(A^o)^2$. The surface-free energy of a solid containing only $CH_2$ groups, $\gamma_{CH2}$, is computed as a function of temperature as follows:

$$\gamma_{CH2} = 36.80 - 0.058\ t \tag{7}$$

where t is the temperature in °C.

Table 11 compares the dispersive surface energy of the 100% AP to that of 100% PHBA and three compositions of blends at 80-120 °C. $\gamma^s_d$ values of the pure AP and PHBA are comparable to each other when blended; the values did not change when AP was still a dominant host polymer. When more PHBA was added, the dilution effect started to show a reduction in $\gamma^s_d$ values, particularly when AP was only 25% in the blend. These results are in agreement with the interaction parameters, $\chi^{-}_{23}$, and the degree of crystallinity, indicating that the affinity of the polymer pair to each other is modest at best.

## 5. CONCLUSIONS

IGC was able to assess the strength of the interactions of 27 solutes having a different chemical nature with three compositions of high molar mass AP blended with a modest molar mass PHBA. The blends' morphology changes, AP-PHBA interactions, degree of crystallinity and the dispersive component of the surface energy, all agreed well with our finding that the affinity of AP to PHBA is modest. IGC was found to be capable of determining those characteristics of a complex polymeric system. It complemented the DSC method in obtaining the $T_m$ values of AP in the blend. The effect of the chemical nature of solutes on $\chi_{1\text{-blend}}$ and $\chi'_{23}$ was evident. These thermodynamic quantities were successfully corrected to yield new quantities, $\chi'_{1\text{-blend}}$ and $\chi^{-}_{23}$, consistent among the different solutes. These parameters' value hovered around the zero mark, indicating modest exothermicity was produced due to the blending process.

The degree of crystallinity of AP decreased as more of PHBA, as a diluent, was added. This explains the low values of the dispersive component of surface energy found by IGC and the decrease in $\gamma^s_d$ values when AP was blended with PHBA.

## CONFLICT OF INTEREST STATEMENT

There is no conflict of interest of any kind.

## Appendix A

The specific retention volume $V_g^o$ depends on several measured chromatographic quantities which makes it the key term in the analysis of IGC experiments. These chromatographic quantities are: the flow rate of the carrier gas, column temperature, retention time of solutes, mass of the polymer, and the pressures of the carrier gas at the inlet and the outlet of the column. $V_g^o$ can be calculated as follows:

$$V_g^0 = \frac{(V_r - V_0)}{w} = \frac{V_N}{w} \qquad \text{(A1)}$$

where $V_r$ is the solute elution volume (Eqn. 3), $V_o$ is the column void volume and $V_N$ is the net retention volume ($V_r$ – $V_o$), $w$ is the mass of the polymer as a stationary phase on the column. Air is used as a non-interacting marker to account for the dead volume ($V_o$) in the chromatographic column when the thermal conductivity (TC) detector is used. $F$ is the flow rate of the carrier gas measured at the column temperature $T_c$, and $w$ is the mass of the stationary phase. Since $\Delta t$ is the difference in retention times of the solute and the marker, it is a function of the flow rate, $F$. Then, the product of $\Delta t$ and the flow rate $F$ may also yield a valuable quantity, the net retention volume, $V_N$, as follows:

$$V_N = \Delta t.F \qquad \text{(A2)}$$

The solute elution volume, $V_r$, data were all obtained by integrating the chromatographic peak maximum positions for solutes, $t_p$.

$$V_N = t_p.F.J \qquad \text{(A3)}$$

$V_N$ in Eqn. (A2) accounts for the retention time of solute in terms of volume in mL and it is dependent on the mass of the polymer in the column. $J$ in eqn. (A3) is the compressibility factor across the column routinely used in GC. To be more specific, $V_N$ can be taken a step further by dividing it by the mass of the polymer and reference it to 0 °C to become a specific retention volume of the solute, $V_g^o$ as given in Eqn. (A4).

$$V_g^o = V_N\left(\frac{273.15}{w.Tc}\right) \qquad \text{(A4)}$$

$V_g^o$ also enables the calculations of the partition coefficient, $K_p$, which will lead to the calculation of the molar free energy of adsorption ($\Delta G_s$) of the solutes into the polymer layer, using the following relationship:

$$K_p = \frac{V_g^o \rho T}{273.12} \qquad \text{(A5)}$$

where $\rho$ is the density of the polymer in the chromatographic column. Then, the relationship between $K_p$ and the $\Delta G_s$ is well known:

$$\Delta G_s = -RT \ln K_p \qquad \text{(A6)}$$

Accordingly, the molar heat of sorption ($\Delta H_s^1$) of solutes into the polymer layer can also be derived from IGC data using the Clapeyron equation, when liquid-vapor equilibrium is established between the injected solute and the stationary phase, as follows:

$$\frac{dP}{dT} = \frac{\Delta H_{ad}^1}{T\left(V_g^- - V_1^-\right)} \qquad \text{(A7)}$$

Here $\overline{V}_g$ and $\overline{V}_l$ are partial molar volumes of the gaseous solute and liquid stationary phase and $\Delta H_{ad}^1$ is the partial molar heat of adsorption of the solute onto the polymeric surface. An analogous relation can be derived for sorption of solutes into the polymer layer ($\Delta H_s^1$):

$$\frac{\partial P_1}{\partial T} = \frac{\Delta H_s^1}{T\left(V_g^- - V_1^-\right)} \qquad \text{(A8)}$$

Considering that $\overline{V}_l$ is negligible as compared to $\overline{V}_g$ and substituting the pressure of the vapor from the ideal gas equation for $P_1 = \frac{RT}{V_g^-}$ (this is always allowed in IGC at infinite solution), Eqn. (A9) can be derived as:

$$d \ln V_g^o . d\left(\frac{1}{T}\right) = -\frac{\Delta H_s^1}{R} \qquad \text{(A9)}$$

A plot of ln $V_g^o$ versus the inverse of temperature will determine $\Delta H_s^1$. If the polymer surface is amorphous at the temperature used in experiment, the equilibrium between the vapor and the polymer will be established; then the slope of the linear relationship can be measured.

$$\Delta H_s^1 = -\left[\frac{R\partial \ln V_g^o}{\partial\left(\frac{1}{T}\right)}\right] \tag{A10}$$

To calculate the interaction parameter $\chi_{12}$ of each solute with the pure polymer, $V_g^o$ from Eqn. (A1) has to be utilized, for the AP-solute, PHBA-solute and blend-solute systems, as follows:

$$\chi_{12} = \ln\frac{273.15R\nu_2}{V_g{}^oV_1P_1^o} - 1 + \frac{V_1}{M_2\nu_2} - \frac{B_{11}-V_1}{RT}P_1^o \tag{A11}$$

$\chi_{12}$ parameter can reveal the strength of the specific interactions between the solutes and the pure polymers and with the polymer pair. Subscript 1 denotes the solute and 2 denotes the polymer under examination; $\upsilon_2$ is the specific volume of the polymer at the column temperature $T_c$; $M_1$ is the molecular weight of the solute; $P_1^o$ is the saturated vapor pressure of the solute; $V_1$ is the molar volume of the solute; $R$ is the gas constant; and $B_{11}$ is the second virial coefficient of the solute in the gaseous state. Equation (A11) represents the residual free energy parameter of binary interaction, $\chi_{12}$, as expressed by Flory-Huggins theory and it is used for routine chromatographic calculations [35, 36].

As we reported in our previously published series of papers [1-3], when two polymers are blended, Eqn. (A11) can be applied to AP and PHBA, designated as polymer 2 and 3, respectively, for given selections of solutes giving $\chi_{12}$ and $\chi_{13}$. In this case, the key term in determining the miscibility of a polymer pair is the free energy of mixing, $\Delta G_{mix}$ as:

$$\Delta G_{mix} = RT[n_1\ln\phi_1 + n_2\ln\phi_2 + n_3\ln\phi_3 + n_1\phi_2\chi_{12} + n_1\phi_3\chi_{13} + n_2\phi_3\chi_{23}] \tag{A12}$$

where $\varphi_i$ and $n_i$ are the volume fractions and the number of moles of the pertinent system components, and $\chi_{ij}$ are the binary interaction coefficients. For a polymer blend containing a pair of polymers (2 and 3), the interaction coefficient will be referred to as $\chi_{23}$ parameter. Since this parameter contains the large molar volume of the polymer ($V_2$), a related parameter can be derived:

$$\chi_{23}' = \left(\frac{V_1}{V_2}\right)\chi_{23} \tag{A13}$$

The $\chi_{23}'$ parameter in Eqn. (A13) can be evaluated as:

$$\chi_{23}' = \left(\frac{1}{\phi_2\phi_3}\right)[\phi_2\chi_{12} + \phi_3\chi_{13} - \chi_{1-blend}] \tag{A14}$$

where $\chi_{1\text{-blend}}$ is the interaction parameter of the solute blend system (subscripted ‘1’ denotes the solute and ‘blend’ denotes the pair of polymers). The term $\chi'_{23}$ in Eqn. (A14), is the interaction between the two polymers (‘2’ and ‘3’) and it is an indicator of the miscibility of a polymer blend. If $\chi'_{23}$ is negative, then the polymer pair is miscible. Recognizing that for a polymer blend containing polymer 2 and polymer 3, $\upsilon_2$ in Eqn. (A11) should be replaced by ($w_2\,\upsilon_2 + w_3\,\upsilon_3$), where $w_2$ and $w_3$, $\upsilon_2$ and $\upsilon_3$ are the weight fractions and the specific volumes of the two polymers in the blend, respectively. Then Eqn. (A14) can be simplified as:

$$\chi_{23}' = \frac{\ln\dfrac{V^0_{g,blend}}{W_2\nu_2 + W_3\nu_3} - \phi_2\ln\dfrac{V^0_{g,2}}{\nu_2} - \phi_2\ln\dfrac{V^0_{g,3}}{\nu_3}}{\phi_2\phi_3} \tag{A15}$$

Eqn. (A15) was first derived by us [22], and $\varphi_2$ and $\varphi_3$ are the volume fractions of the two polymers in the blend. To obtain $\chi'_{23}$ for a polymer blend, utilizing IGC, $\chi_{12}$ and $\chi_{13}$ have to be known for pure polymers 2 and 3. Three columns are usually prepared; two from the pure polymers (2 and 3) and the third from a blend of the polymer pair (blend). Furthermore, three more columns containing different compositions of the blend can also be prepared if the effect of the weight fraction of the blend on the miscibility needs to be explored. These columns were studied under identical conditions of column temperature, carrier gas flow rate, inlet pressure of the carrier gas, and using the same solutes. Thus, at high molecular weights, only a negative $\chi'_{23}$ parameter satisfies the condition for miscibility of a polymer pair.

## Appendix B

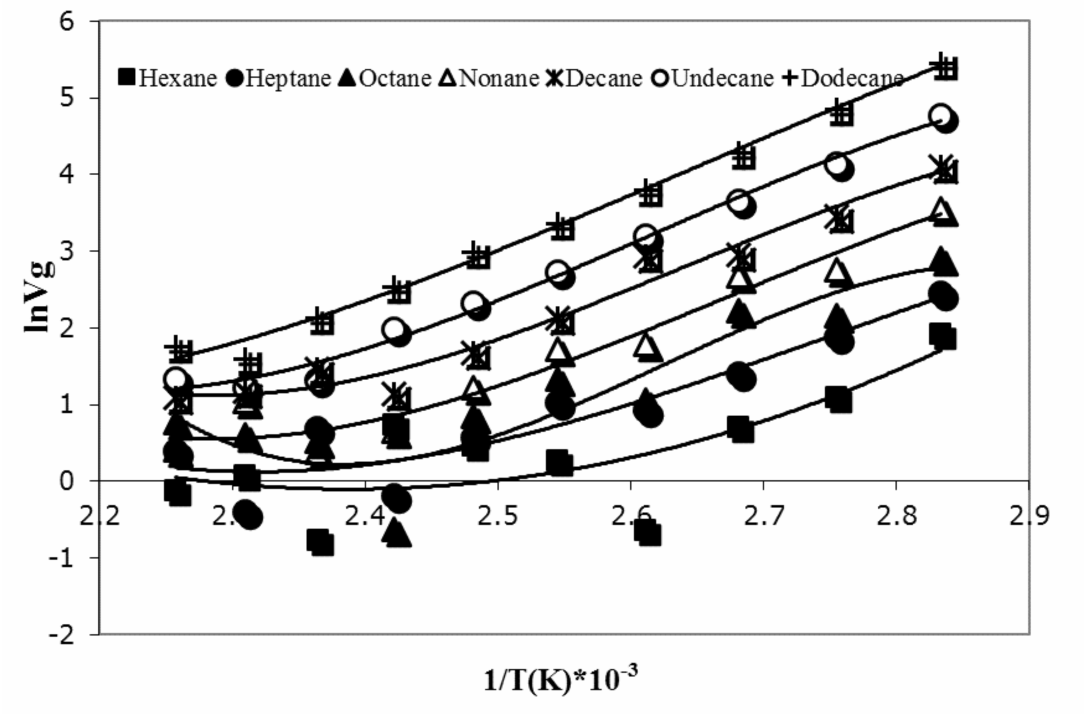

**Figure B1.** Retention Diagram of Alkane-Blend of (25% PHBA-75% AP) (80-170°C).

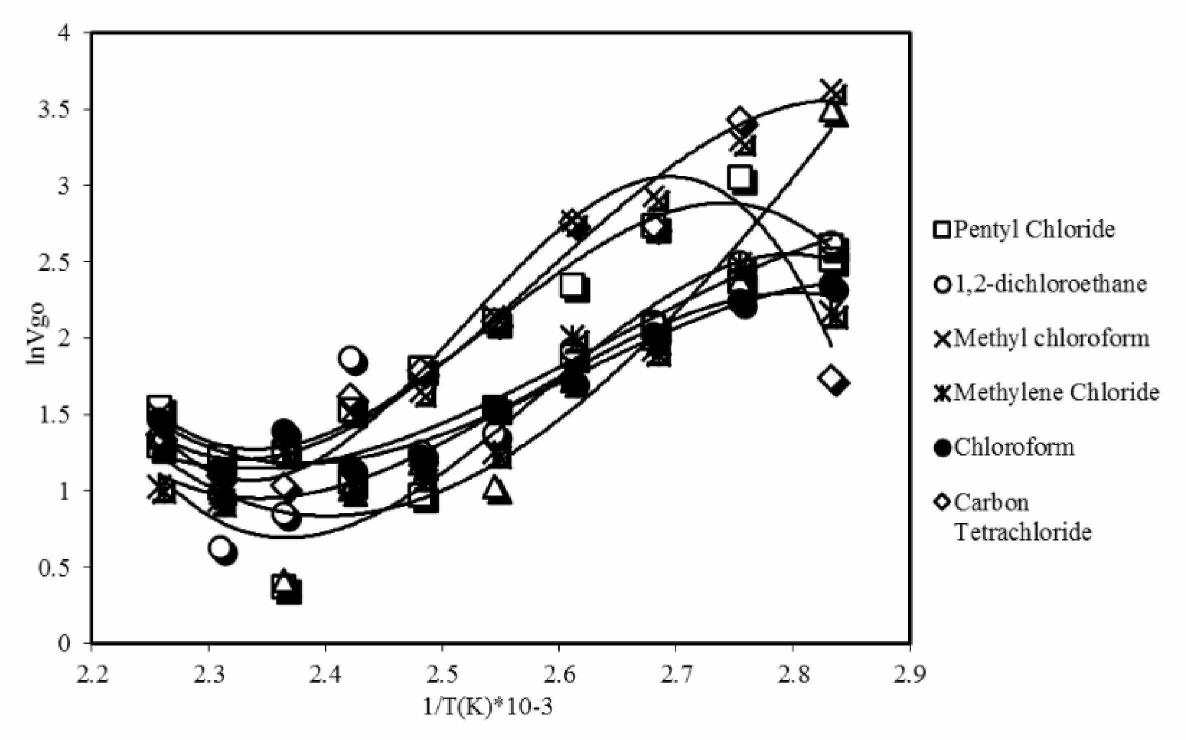

**Figure B2.** Retention Diagram of Halogenated-Blend of (25% PHBA-75% AP) (80-170°C).

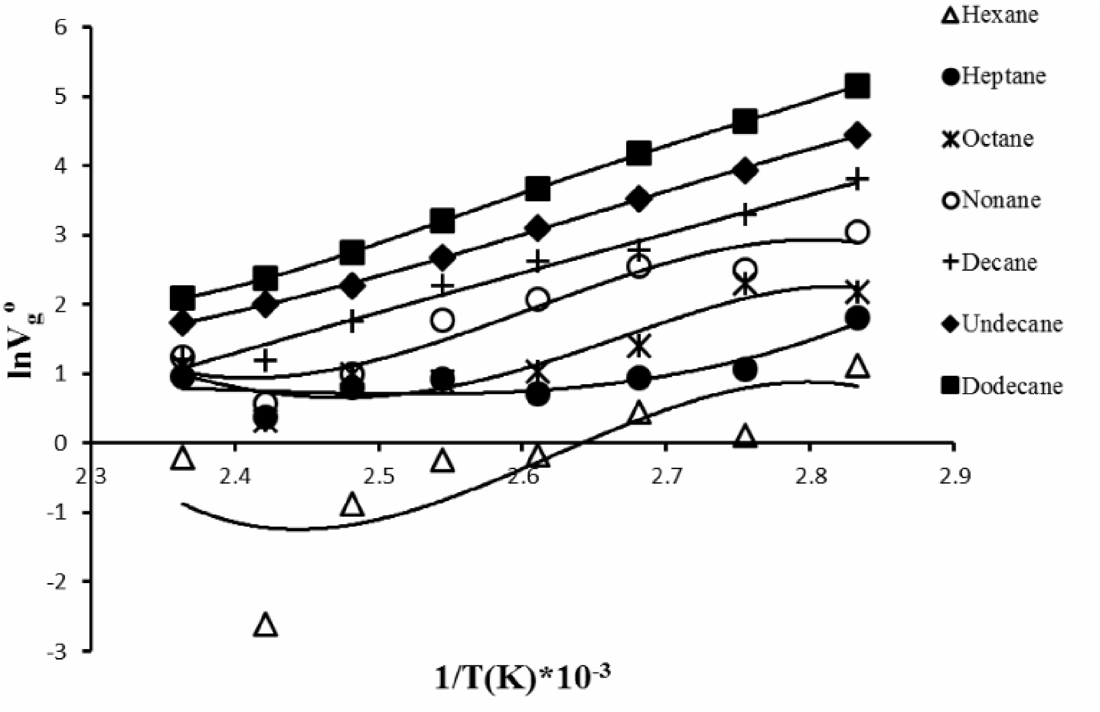

**Figure B3.** Retention Diagram of Alkane-Blend of (50% PHBA-50% AP) (80-170°C).

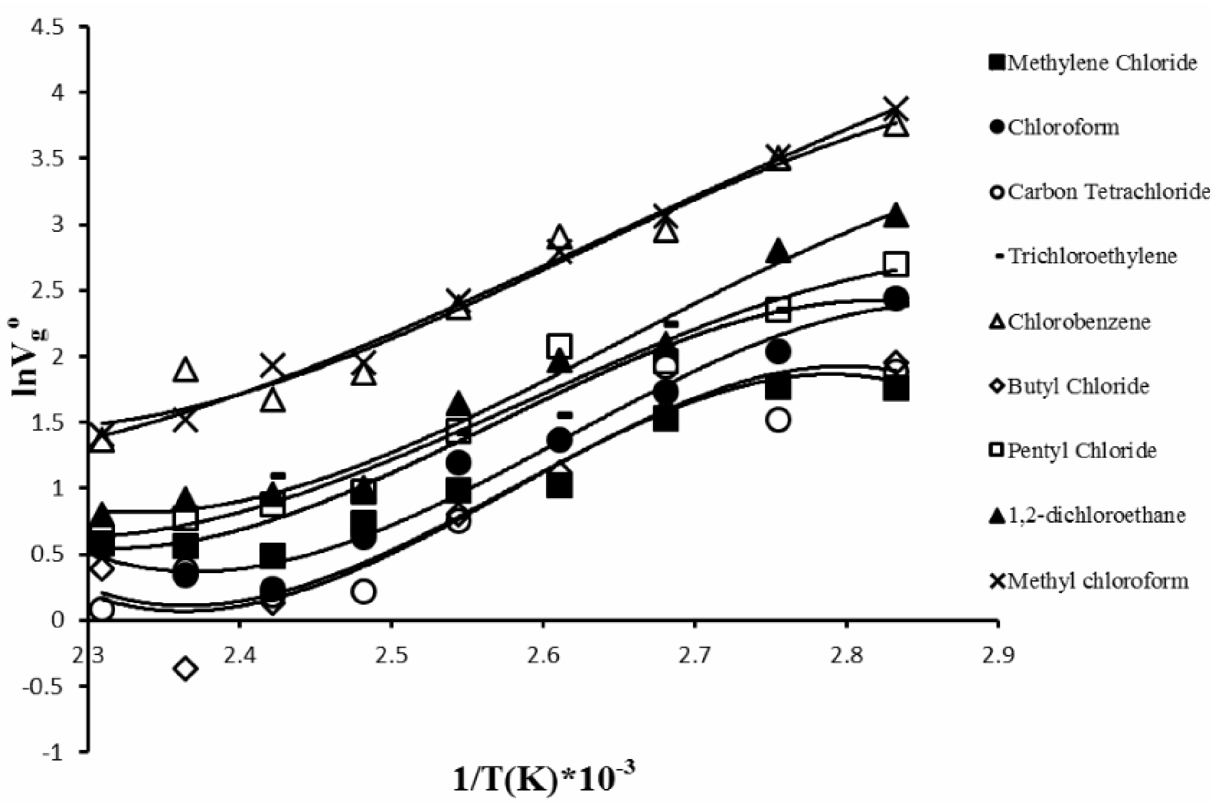

**Figure B4.** Retention Diagram of Halogenated-Blend of (50% PHBA-50% AP) (80-170°C).

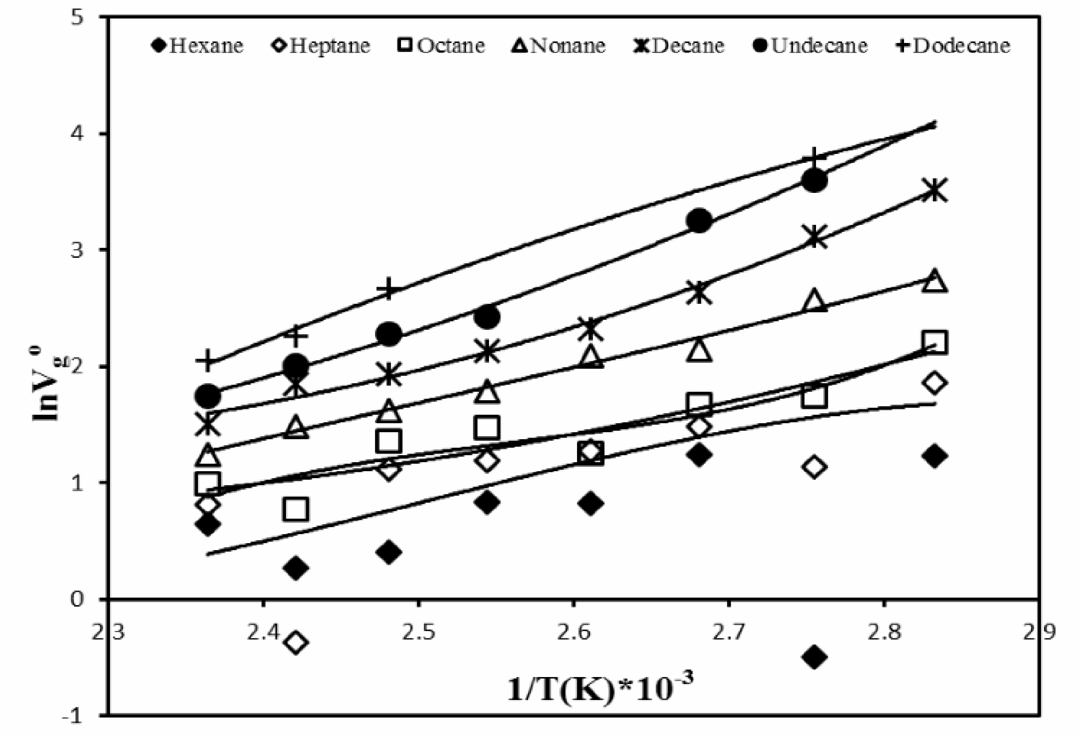

**Figure B5.** Retention Diagram of Alkane-Blend of (75% PHBA-25% AP) (80-170°C).

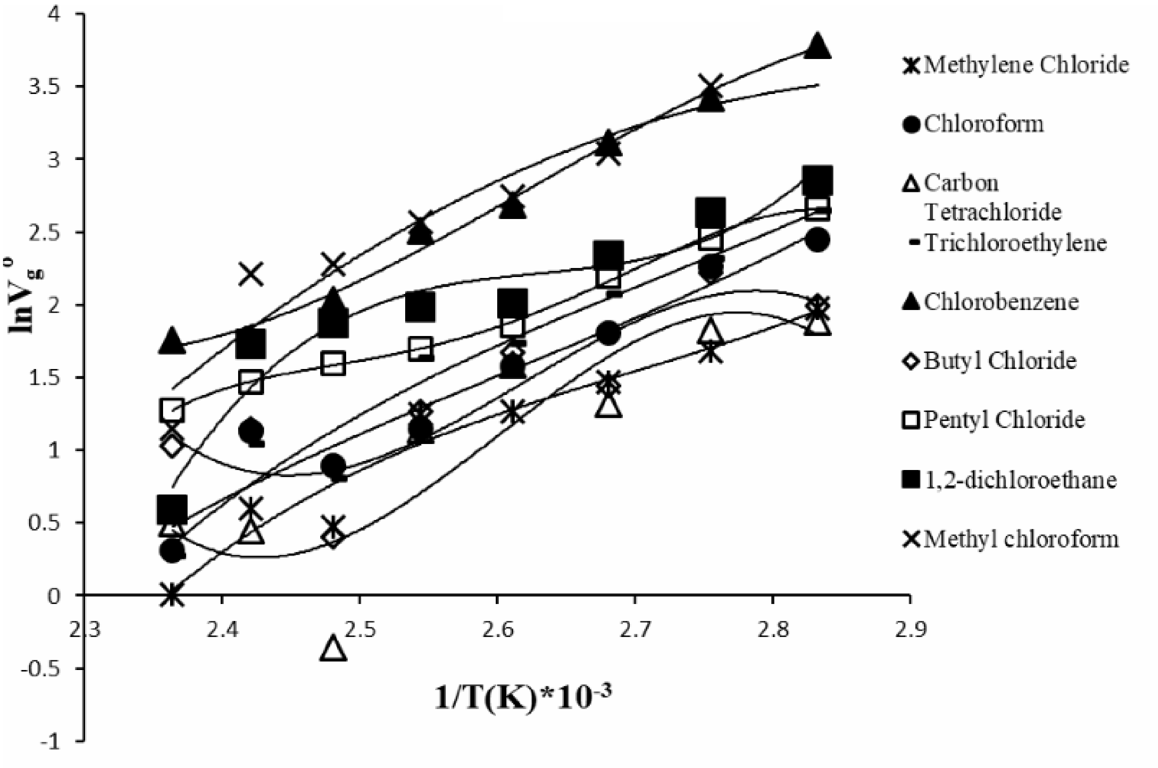

**Figure B6.** Retention Diagram of Halogenated-Blend of (75% PHBA-25% AP) (80-170°C).

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