

New Methods to Characterize the Surface and Interface Acid-Base Properties of Polylactides Polymers by Inverse Gas Chromatography

Carla Zarazir^{1,2}, Mohamad Rajab^{1,2}, Houssam Obeid^{1,2}, Joumana Toufaily^{1,2}, Imad Toufeili³ and Tayssir Hamieh^{1,2*}

¹Laboratory of Materials, Catalysis, Environment and Analytical Methods Laboratory (MCEMA), Lebanese University, Lebanon

²Laboratory of Applied Studies to the Sustainable Development and Renewable Energies (LEADDER), EDST, Lebanese University, Lebanon

³Department of Nutrition and Food Sciences, American University of Beirut (AUB), Lebanon

ARTICLE INFO

Received Date: June 15, 2022

Accepted Date: July 26, 2022

Published Date: July 28, 2022

KEYWORDS

Free energy of Adsorption
Specific enthalpy and entropy
Lewis acid and base constants
Donor and acceptor number of electron
Glass transition
Hamieh's model

Copyright: © 2022 Tayssir Hamieh et al., Chromatography And Separation Techniques Journal. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Citation for this article: Carla Zarazir, Mohamad Rajab, Houssam Obeid, Joumana Toufaily, Imad Toufeili and Tayssir Hamieh. New Methods to Characterize the Surface and Interface Acid-Base Properties of Polylactides Polymers by Inverse Gas Chromatography. Chromatography And Separation Techniques Journal. 2022; 3(1):123

Corresponding author:

Tayssir Hamieh,
Laboratory of Materials, Catalysis, Environment and Analytical Methods Laboratory (MCEMA), Lebanese University, Lebanon,
Email: tayssir.hamieh@ul.edu.lb

ABSTRACT

The thermodynamic and acid base properties of some polymeric materials such as polylactides used in many industrial applications were determined by using the inverse gas chromatography technique at infinite dilution. Retention volume of the injected organic probes into the chromatographic column containing the investigated polymer was obtained by using this powerful technique. The curves $RT \ln V_n = f(1/T)$ of n-alkanes adsorbed on polymer surface allowed us to determine with an excellent accuracy the glass transition temperature of polylactide polymer. It was proved the glass transition temperature of this polymer is equal to 64 °C for all used n-alkanes. Many methods were used in literature to characterize the surface properties of polymers. The difficulty to know with accuracy the surface area of n-alkanes and polar molecules prevented us to use Fowkes method. Saint-Flour and Papirer method was used to evaluate the specific interactions and acid-base properties in the Lewis terms of polylactides by using the variations of the specific free energy of adsorption of polar probes adsorbed on the polymers as a function of the temperature and determining the specific enthalpy and entropy of adsorption of polylactide polymer. This study proved that the Gutmann method could not be used, because of non-linearity of the specific enthalpy as a function of the acid-base constants of the polymer substrates (linear regression coefficient $r^2 \ll 1$). The acid-base constants K_A , K_D and the amphoteric constant K of polylactides surfaces were determined using Hamieh's model.

INTRODUCTION

Polylactides have been playing a major role in many applications such as medical science, biotechnology and food science due to their biocompatibility and biodegradability [1]. These polymers can be obtained from a renewable agricultural source such as corn or starch, they provide significant energy savings, they are recyclable and compostable and they have the ability to decompose into naturally occurring metabolites via hydrolysis or enzymatic processes [2,3]. Several studies have demonstrated that the amount of lactic acid that migrates into foodstuff from

packaging materials is low. Therefore, polylactide polymers may be good candidates for packaging applications [4,5]. Poly Lactic Acid (PLA) could be used as alternatives to synthetic plastic such as Polyethylene Terephthalate (PET), High Density Polyethylene (HDPE), Polypropylene (PP) and Polyvinyl Chloride (PVC) to solve the ecological problem of plastic waste accumulation [6]. Lactic acid based polymers are presumed to have inferior performance to conventional plastics, but the mechanical properties (elasticity and stiffness) of PLA is comparable to petroleum-based plastics such as PET [6,7]. It is well-known that the surface properties of polymer materials, and especially, the Lewis acid base properties can be determined by inverse gas chromatography technique that can also allow to obtain the adsorption thermodynamic parameters as specific free energy, enthalpy and entropy of adsorption, Lewis acid–base character of the surface, surface Nano roughness parameter etc., [8-11].

Inverse Gas Chromatography (IGC) is an important technique to characterize the surface properties (surface energy, heat of adsorption, and specific interaction of adsorption) of materials [12-18] and recently pharmaceuticals [19-34]. In many previous studies [35-46], we used Inverse Gas Chromatography (IGC) to characterise the surface characteristics of various oxides and polymers, especially, their surface energies and their interactions with some organic molecules. The transition temperatures of polymers and the acid-base properties of solid materials or nanomaterials were also determined by IGC technique [40-46].

The Inverse Gas Chromatography (IGC) technique at infinite dilution was mostly used in literature by using Saint-Flour and Papirer's approach [44-46] and Hamieh's model [47-49] to determine the specific free enthalpy and enthalpy of adsorption and the acid-base constants of the polymer or oxide materials. The objective of this paper is to determine, by IGC technique at infinite dilution, the surface physicochemical properties of polylactide polymers and more particularly, to appreciate the glass transition temperature the surface and specific enthalpy and entropy of polar probes adsorbed on polylactide polymers. This will allow determining the acid-base constants K_A , K_D and the amphoteric constant K in Lewis terms of the above polymers.

In the following section, we give some details on the theory and models of the Inverse Gas Chromatography at Infinite Dilution (IGC-ID). We applied this technique in the experimental part to determine the specific interactions and acid-base constants of polylactide polymer.

THEORY AND METHODS

Inverse gas chromatography has been used for many years to determine the superficial phenomena, and acid-base properties of solid materials [35-56]. We applied this technology to determine the changes, as a function of temperature, of the superficial properties of polylactide polymers. Probes of known properties are injected into the column containing the solid. The retention times of these probes, measured at infinite dilution, allow us to determine the interactions between model organic molecules and the solid, if we assume there is no interaction between the probe molecules themselves. Measurements will be carried out with a GC FID chromatograph equipped with a flame ionization detector of high sensitivity. The data retention will be obtained with a stainless steel column 15-30 cm long and 2 mm internal diameter packed with 1-2 g of solids in powder forms.

Retention volume

The net retention volume V_n which serves to determine the thermodynamic quantities, it is the volume of carrier gas through the column since the introduction of the probe until the output of the maximum of the peak of the inferred methane retention volume V_0 . It is influenced by the retention time according to the following relation:

$$V_n = j D_c (t_r - t_0) \quad (1)$$

Where t_r is the retention time of the probe, t_0 the zero retention reference time measured with a non-adsorbing probe such as methane, D_c the flow rate and j a correction factor taking into account the compression of the gas [56].

Specific interactions

The free energy of adsorption ΔG^0 of n-alkanes on the solid substrates is given by the following fundamental equation of IGC technique:

$$\Delta G^0 = RT \ln V_n + C \quad (2)$$

Where R is the ideal gas constant, T the absolute temperature and C a constant depending on the reference state of adsorption. The free energy of adsorption ΔG^0 contains the

two contributions relative to the dispersive and specific interactions. In the case of n-alkanes, ΔG^0 is equal to the free energy of adsorption corresponding to the dispersive interactions ΔG^d only. To calculate the specific interactions between the solid substrates and polar probes, several methods were used in the literature [12-15,35-56]. Two methods are presented below. The method developed by Brendlé and Papier [44,45] can be used to quantify more precisely the specific interactions, method considered up to now the most popular one.

Proposed methods

This method allowing to obtain specific enthalpy of interaction between a probe and a solid is that developed by Papierer team [44-46] who obtained a straight line when plotting $RT \ln V_n$ against the logarithm of the vapor pressure $\ln P_0$ where P_0 is the vapor pressure of the probes. For a homologous series of n-alkanes, whatever the nature of the solid substrates:

$$RT \ln V_n = A \ln P_0 + B \quad (3)$$

Where A and B are constants depending of the nature of the solid substrate.

When polar molecules are injected into the column, specific interactions are established between these probes and the solid surface and ΔG^0 is now given by:

$$\Delta G^0 = \Delta G^d + \Delta G^{sp} \quad (4)$$

Where ΔG^{sp} refers to specific interactions of a polar molecule adsorbed on solid substrate.

The choice of Papierer method was made considering that the logarithm of the vapor pressure which is closely related to the evaporation enthalpies (ΔH_v) was representative of the capacity of interactions of two identical molecules. This method presents several advantages since P_0 values are given in the literature or are computable even at relatively high measurement temperatures as long as these stay below the critical temperature of the probe. Yet, problems do appear with certain solids, possessing a high surface energy, since the representative points of some polar probes fall beneath the alkane-line. We advantageously used Papierer method to quantify the specific free energy of adsorption of polar molecules and obtain the acid-base constants of the different hydrocarbon materials.

Determination of acid-base constants of solid substrates

By plotting ΔG^{sp} of the polar molecules as a function of the temperature, the specific enthalpy

(ΔH^{sp}) will be obtained from:

$$\Delta G^{sp} = \Delta H^{sp} - T \Delta S^{sp} \quad (5)$$

The curves representing the variations of $\Delta G^{sp}(T)$ versus the temperature will allow the thermodynamic calculation of specific enthalpy and entropy as a function of the temperature.

The Guttmann method: Inverse gas chromatography is used to evaluate Lewis type acid- base interactions, exchanged between a solid surface and polar molecules. Guttmann [56] classified the polar molecules by assigning an Electron Donor (ND) and a number of Electron Acceptor (NA) which realizes respectively the acidity and the basicity of the molecule. In analogy to the approach of Guttmann, Papierer and al [44-46] proposed to characterize the solid by two parameters K_A and K_D respectively reflect the basic and the acidic character of the solid. These two constant measure the ability of the solid to develop respectively the acid and base interactions with basic, acidic or amphoteric probes. They are connected to the specific enthalpy ΔH_o^{sp} through the following equation:

$$(-\Delta H^{sp}) = (K_A \cdot DN + K_D \cdot AN) \quad (6)$$

Where K_A and K_D respectively represent the acidic and the basic character of the solid and NA and ND represent the donor number and the electron acceptor of the probe according to the scale of Guttmann [57].

Equation 6 can be written as:

$$\frac{-\Delta H^{sp}}{AN} = \frac{DN}{AN} K_A + K_D \quad (7)$$

The representation of $\frac{-\Delta H^{sp}}{AN}$ in function of $\frac{DN}{AN}$ gives in general a straight line of slope K_A and intercept K_D

The Hamieh model: In several cases, the Guttmann method cannot be applied because the linearity of equation 6 is not satisfied for many solid substrates. Hamieh et al., [41-44,47-49] corrected the classical relationship and proposed a new equation by adding a third parameter K reflecting the amphoteric character of the oxide or polymer according to:

$$(-\Delta H^{sp}) = K_A DN + K_D AN - K DN AN \quad (8)$$

By dividing by AN , we obtain:

$$-\frac{\Delta H^{sp}}{AN} = K_A \frac{DN}{AN} + K_D - K \cdot DN \quad (9)$$

Equation (13) can be symbolically written as:

$$X_1 = K_D + K_A X_2 - K X_3 \quad (10)$$

Where $X_1 = -\frac{\Delta H^{sp}}{AN}$, $X_2 = \frac{DN}{AN}$, $X_3 = DN$ and $K =$

$K(K_A, K_D)$

X_1 , X_2 and X_3 are known for every polar molecule, whereas K_D , K_A and K are the unknown of the problem.

By using N probes, relationship (10) will allow us to obtain a linear system given three equations at three unknown numbers: K_D , K_A and K . The matrix representing this linear application is a symmetrical one; we deduce that the problem (10) has a unique solution for $N \geq 3$. We can apply this method to calculate the acid-base constants of our silicas materials.

EXPERIMENTAL PART

Materials

PLA polymers used in the storage of olive oils were procured directly from Lebanese markets. The packaging polymer samples were cut into small rectangular pieces with scissors and using cotton gloves to avoid contamination of the plastic samples. The area of each test specimen was equal to 10 cm². The polymer pieces were then grinded to obtain a size range of PLA particles between 100 and 250 μm. Particles of the correct size were introduced into a stainless steel column, which was 30 cm long and had an internal diameter of 2 mm. A mass of 1 g of PLA was used to fill the chromatographic column. The column filled with the sample was conditioned at 120 °C for 12 h to remove any impurities.

The measurements of retention time were done by using the IGC technique. The column was then attached to the gas chromatograph, fitted with a flame ionization detector. Helium was used as carrier gas; its flow-rate was equal to about 20 mL min⁻¹. IGC measurements at infinite dilution were done by varying the temperature from 40 °C to 100 °C.

Chromatographic injections were made using Hamilton micro syringes. We used the inverse gas chromatography technique at infinite dilution for the physicochemical characterization of different materials. Measurements were carried out with a DELSI GC 121 FB Chromatograph equipped with a flame ionization detector of high sensitivity.

Solvents

Classical organic probes, characterized by their donor and acceptor numbers, were used in this study. Corrected acceptor number $AN' = AN - AN^d$, given by Riddle and Fowkes [51], who subtracted the contribution of Van der Waals interactions (or dispersion forces), was normalized by Hamieh et al., [47,48], and proposed a dimensionless donor number DN' according to the following relationship:

$$DN' = 2.5(\text{mol/kcal}) DN (\text{kcal/mol}) \quad (11)$$

However, if one wants to use DN in kcal/mol, AN' can be easily transformed to the kcal/mol unit using the following relationship:

$$AN'(\text{kcal/mol}) = \frac{40 (\text{kcal/mol})}{100} AN' (\text{unitless}) \quad (12)$$

Solvents listed below were used as probes for IGC measurements. They were selected for their ability to interact with three different types of interaction forces, that is, dispersive, polar, and hydrogen bonding. All probes (Aldrich or Merck) were highly pure grade (i.e., 99%). The probes used were n-alkanes (pentane, hexane, heptane, octane, and nonane); amphoteric solvents: acetone, toluene; basic solvents: ethyl acetate, and higher acidic solvent: dichloromethane. (Table 1) gives donor and acceptor numbers [57,58] of probe solvents used in this study.

Table 1: Normalized donor and acceptor numbers of some polar molecules.

Polar probes	DN'	AN'	DN'/AN'	Character
Dichloromethane	3	13.5	0.22	Higher acidity
Benzene	0.25	0.6	0.42	Weaker acidity
Toluene	9.75	3.3	2.95	Amphoteric
Acetone	42.5	8.7	4.89	Amphoteric
Ethyl acetate	42.8	5.3	8.08	More basic

GC Conditions

The IGC measurements were performed on a commercial Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector. Dried nitrogen was the carrier gas. The gas flow rate was set at 30 mL/min. The injector and detector temperatures were maintained at 200 °C during the experiments. To achieve infinite dilution, 0.5 μL of each probe

was injected with 10 μL Hamilton syringes, in order to approach linear condition gas chromatography. In such a way that the interactions between probe molecules can be considered to be negligible and only the interactions between the surface of the solid and an isolated probe molecule are important. The column temperatures were 40 to 100 $^{\circ}\text{C}$, varied in 5 to 10 $^{\circ}\text{C}$ steps. Each probe injection was repeated three times, and the average retention time, t_R , was used for the calculation. The standard deviation was less than 1% in all measurements. All four columns used in this study were prepared using a stainless-steel column with a 5 mm inner diameter and with an approximate length of 30 cm.

Results and discussion

Determination of the glass transition temperature of PLA by IGC:

The results obtained with PLA powder by IGC at infinite dilution allowed to determine the retention volume of different n-alkanes and polar molecules adsorbed on PLA polymers. On figure 1, we plotted the curves $RT\ln V_n = f(1/T)$ of PLA for the different n-alkanes obtained by IGC at infinite dilution. The curves of (Figure 1) clearly shows the presence of a glass transition $T_g = 64^{\circ}\text{C}$ (see on figure 1, $1/T_g = 0.00297\text{ K}^{-1}$). The usual glass transition of PLA is equal to 60 $^{\circ}\text{C}$. However, this value can vary between 60 $^{\circ}\text{C}$ and 65 $^{\circ}\text{C}$, because the glass transition is very affected by the experimental method, experimental conditions, the molecule nature and the polymer morphology.

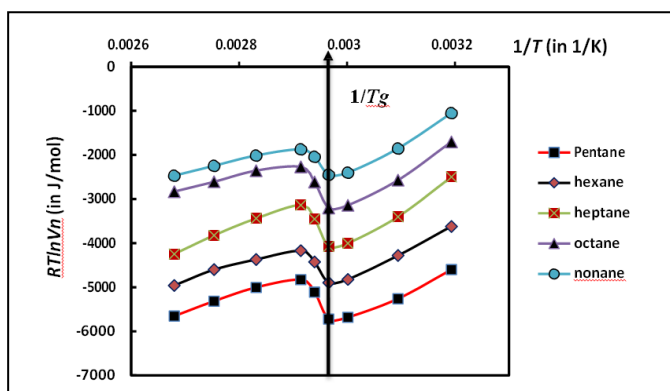


Figure 1: Variation of specific $RT\ln V_n$ (in J/mol) of n-alkanes adsorbed on PLA polymer as a function of the inverse of the temperature ($1/T$).

Variations the specific free energy changes of PLA: In this part, we give on (Figure 2) the variations of specific free energy changes ($-\Delta G^{sp}$) of PLA polymers surfaces in interaction with the different adsorbed polar molecules as a function of

the temperature T . The specific free energy changes are obtained by using relations 3 and 4. The curves of figure 2 show for all polar probes adsorbed on PLA polymer a linear dependency in the temperature intervals [313K – 333K] and [353K – 373K] (see dashed lines). However, the linearity is not satisfied near the glass transition temperature T_g in the domain [333K – 353K] where the specific interaction free energy presents a maximum at this temperature T_g for all polar molecules. This will induces a large variation of specific interactions as a function of the temperature and consequently an important dependency of acid base properties of PLA versus the temperature. The large specific interactions are obtained with the dichloromethane molecule, the more acidic probe. This reveals more basic PLA polymer than acidic. On the other hand, there are important specific interactions with the amphoteric probes, such as toluene and acetone meaning an important acid base character of PLA surface in Lewi terms.

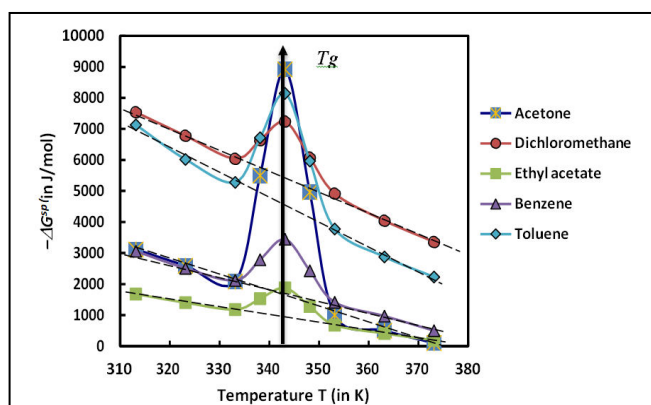


Figure 2: Evolution of specific free energy ($-\Delta G^{sp}$) of the different polar probes adsorbed on PLA polymer as a function of the temperature T .

Variations of the specific enthalpy ΔH^{sp} and entropy ΔS^{sp} of

PLA: The curve equations ($-\Delta G^{sp}(T)$) obtained from figure 2 for the different domains of temperature given on (Tables 2–6) also allows to obtain the specific enthalpy ΔH^{sp} and entropy ΔS^{sp} of various polar molecules. Knowing the values of the above specific variables, we obtained the variations of the specific enthalpy ΔH^{sp} and entropy ΔS^{sp} of various polar probes as a function of the temperature. The obtained curves plotted on (Figures 3,4) clearly show the non-linearity of these variables surrounding the glass transition temperature.

Figures 3 and 4 prove that the linearity of specific enthalpy ΔH^{SP} and entropy ΔS^{SP} of various polar probes are satisfied in the temperature intervals [313K – 333K] and [353K – 373K]. However, this linearity is not assured in the interval [333K – 353K] where we clearly observe an important variation of the specific variables near the glass transition temperature.

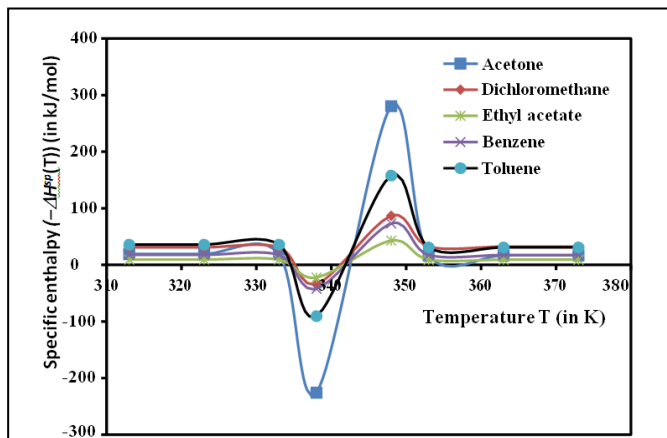


Figure 3: Evolution of specific enthalpy ($-DH^{SP}$) of the different polar probes adsorbed on PLA polymer as a function of the temperature T.

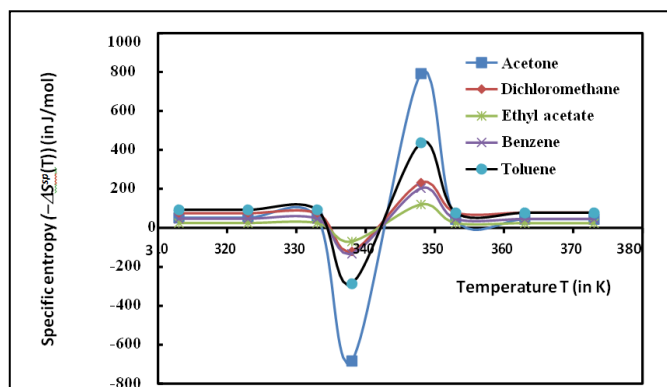


Figure 4: Evolution of specific entropy ($-DS^{SP}$) of the different polar probes adsorbed on PLA polymer as a function of the temperature T.

Determination of the acid base constants of PLA polymer: In order to determine the acid-base constants K_A and K_D of PLA polymer, we represented on (Figure 5) the variation of $-\Delta H^{sp}/AN'$ as a function of DN'/AN' of different polar molecules adsorbed on PLA for the various domains of temperature. The obtained curves of figures 4 demonstrated the non-linearity of the variations of $-\Delta H_{sp}/AN'$ for all temperatures. Consequently, the classical equation (7) cannot be used here to

determine the values of K_A and K_D of these materials, because of the smaller value of the linear regression coefficients between ($r^2 = 0.1$ to 0.2). Therefore, to determine with more accuracy the acid base constants of PLA, we then applied the Hamieh's model and corrected the classic equation (7).

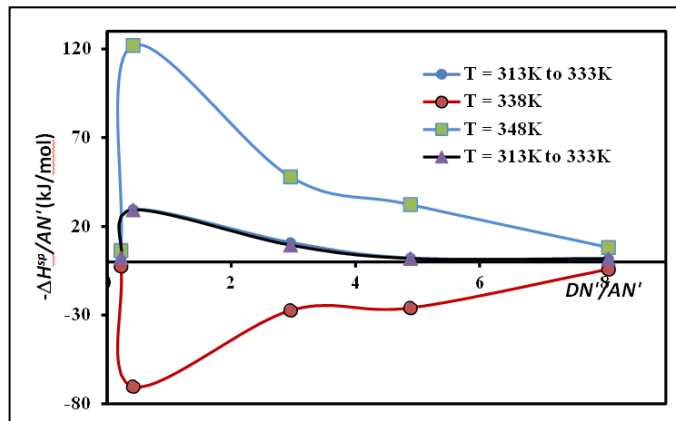


Figure 5: Evolution of $-DH^{SP}/AN'$ (kJ/mol) of polar molecules adsorbed on PLA polymer, versus of DN'/AN' at different temperatures.

Accurate calculation of acid base constant using Hamieh's model and discussion: Hamieh's model [29, 40-42,52] proposed a new relationship by adding a third parameter K reflecting the amphoteric character of solid surfaces (see equation 8). We used this model to calculate the three acid-base constants K_A , K_D and K of PLA surface and obtained an excellent three dimension linear regression coefficients approaching $r^2 = 1.000$. The obtained results are given on (Table 7).

Table 2: Equations of specific free energy ($-\Delta G^{SP}(T)$) and values of specific enthalpy $-\Delta H^{SP}$ and entropy $-\Delta S^{SP}$ of acetone.

Range of T	$-\Delta G^{SP}(T)$ of Acetone	$-\Delta H^{SP}$ (kJ/mol)	$-\Delta S^{SP}$ (J/mol)
313 - 333	$-\Delta G^{SP}(T) = -51.75T +$	19.322	51.75
333 - 343	$-\Delta G^{SP}(T) = 683.64T -$	-225.67	-683.6
343 - 353	$-\Delta G^{SP}(T) = -792.14T +$	280.745	792.14
353 - 373	$-\Delta G^{SP}(T) = -45x +$	16.875	45

The obtained results obtained solving the linear system (10) are presented on figures 6 giving the variations of acid-base constants K_D , K_A , K and of the ratio K_A/K_D of PLA surface as a

function of the temperature. (Figure 6) obviously show that the PLA polymer has a strong that decreases near the glass transition temperature and increases after T_g temperature. PLA presents very weak acid character, whereas the global basic character given by K_D/K_A increases when the temperature increases.

Table 3. Equations of specific free energy ($-\Delta G^{SP}(T)$) and values of specific enthalpy $-\Delta H^{SP}$ and entropy $-\Delta S^{SP}$ of Acetone.

Range of T	$-\Delta G^{SP}(T)$ of Dichloromethane	$-\Delta H^{SP}$ (kJ/mol)	$-\Delta S^{SP}$ (J/mol)
313 - 333	$-\Delta G^{SP}(T) = -75T + 31023$	31.023	75
333 - 343	$-\Delta G^{SP}(T) = 120T - 33938$	-33.938	-120
343 - 353	$-\Delta G^{SP}(T) = -232T + 86851$	86.851	232
353 - 373	$-\Delta G^{SP}(T) = -78T + 32434$	32.434	78

Table 4: Equations of specific free energy ($-\Delta G^{SP}(T)$) and values of specific enthalpy $-\Delta H^{SP}$ and entropy $-\Delta S^{SP}$ of Ethyl acetate.

Range of T	$-\Delta G^{SP}(T)$ of Ethyl acetate	$-\Delta H^{SP}$ (kJ/mol)	$-\Delta S^{SP}$ (J/mol)
313 - 333	$-\Delta G^{SP}(T) = -25T + 9498.9$	9.499	25
333 - 343	$-\Delta G^{SP}(T) = 70T - 22141$	-22.141	-70
343 - 353	$-\Delta G^{SP}(T) = -120.2T + 43127$	43.127	120.2
353 - 373	$-\Delta G^{SP}(T) = -24.4T + 9286.9$	9.287	24.4

Table 5: Equations of specific free energy ($-\Delta G^{SP}(T)$) and values of specific enthalpy $-\Delta H^{SP}$ and entropy $-\Delta S^{SP}$ of Benzene.

Range of T	$-\Delta G^{SP}(T)$ of Benzene	$-\Delta H^{SP}$ (kJ/mol)	$-\Delta S^{SP}$ (J/mol)
313 - 333	$-\Delta G^{SP}(T) = -47T + 17751$	17.751	47
333 - 343	$-\Delta G^{SP}(T) = 133T - 42189$	-42.189	-133
343 - 353	$-\Delta G^{SP}(T) = -203.5T + 73281$	73.281	203.5
353 - 373	$-\Delta G^{SP}(T) = -45.75T + 17576$	17.576	45.8

Table 6: Equations of specific free energy ($-\Delta G^{SP}(T)$) and values of specific enthalpy $-\Delta H^{SP}$ and entropy $-\Delta S^{SP}$ of Toluene.

Range of T	$-\Delta G^{SP}(T)$ of Toluene	$-\Delta H^{SP}$ (kJ/mol)	$-\Delta S^{SP}$ (J/mol)
313 - 333	$-\Delta G^{SP}(T) = -92.5T + 36035$	36.035	92.5
333 - 343	$-\Delta G^{SP}(T) = 287T - 90334$	-90.334	-287
343 - 353	$-\Delta G^{SP}(T) = -437T + 158107$	158.107	437
353 - 373	$-\Delta G^{SP}(T) = -77.5T + 31107$	31.107	77.5

Three acid-base constants K_A , K_D and K of PLA

Temperature	K_D	K_A	K	K_D/K_A
313	19.8	-1.3	-1.1	-15.3
323	19.8	-1.3	-1.1	-15.3
330	19.8	-1.3	-1.1	-15.3
335	12.0	-0.8	-0.7	-15.0
343	-43.4	2.8	1.5	-15.3
353	77.6	-5.0	-3.2	-15.4
363	10.0	0.4	-1.1	23.8
368	4.0	1.0	-0.6	4.1
373	4.0	1.0	-0.6	4.1

Table 8: Values specific enthalpy $-\Delta H^{SP}$ and entropy $-\Delta S^{SP}$ of interaction of polar molecules with the corresponding values of the linear regression

Polar probes	$-\Delta H^{SP}$ (kJ/mol)	$-\Delta S^{SP}$ (J/mol)	r^2
Acetone	20.777	51.228	0.116
dichloromethane	29.217	68.098	0.7921
ethyl acetate	96.58.6	24.835	0.6442
benzene	16.155	40.846	0.6108
Toluene	32.868	80.192	0.5727

Comparison with Gutmann method: By using Gutmann method expressed by equation (7). We calculated the acid base constants, K_D , K_A of PLA polymer. Results obtained allowed us to deduce, from the variation of the specific free energy of adsorption against the temperature ($-\Delta G^{SP}(T)$), the specific enthalpy and entropy of interaction of polar molecules

adsorbed on polylactide polymer (Table 8). It is clear that the linear regression coefficient, r^2 , obtained for the various polar molecules adsorbed on PLA is comprised between 0.11 and 0.79. This implied that the linearity of $(-\Delta G_{sp}(T))$ is not assured. The Gutmann method then cannot be advantageously used in this case. Now, if we use the Gutmann method, we obtain the following figure:

(Figure 7) gave a very poor linear regression coefficient ($r^2 = 0.0003$); the linear equation is given by:

$$(-\Delta H_{sp}/AN') = 0.06 (DN'AN') + 11.8, (r^2 = 0.0003)$$

We deduced the values of acid base constants of PLA by Gutmann method:

$$K_D = 11.8, K_A = 0.06 \text{ and } K_D / K_A = 196.6$$

Therefore, these values cannot be compared to those obtained by using Hamieh's model.

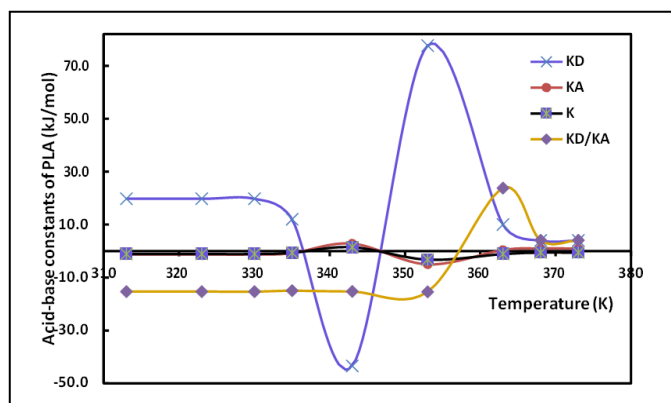


Figure 6: Evolution of acid-base constants K_D , K_A , K and the ratio K_A/K_D (c) of PLA surfaces, versus the temperature T (K).

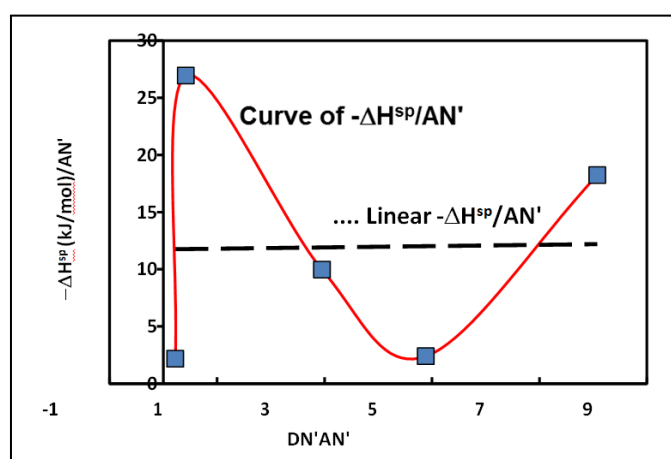


Figure 7: Variations of $-DH^{sp}/AN'$ (kJ/mol) of polar molecules adsorbed on PLA polymer, versus of DN'/AN' .

CONCLUSION

In this paper, we determined the acid base properties of polylactide polymer by using the inverse gas chromatography technique at infinite dilution. This technique allowed us to determine the glass transition of PLA, $T_g = 64$ °C and the specific interactions and acid-base properties in the Lewis terms of PLA. The variations of the specific free energy of adsorption of polar probes adsorbed on the polymers as a function of the temperature were determined and allowed to obtain the specific enthalpy and entropy. This allowed determining with a good accuracy the acid-base constants K_A , K_D and the amphoteric constant K of PLA surface. It was shown that the PLA polymer exhibits a strong basic character in Lewis terms.

FUNDING SOURCES

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

REFERENCES

1. Ahmed J, Varshney SK. (2011). Polylactides — Chemistry, properties and green packaging technology: a review. *International Journal of Food Properties*. 14:37-58.
2. Saltzman WM. (2001). *Drug Delivery: Engineering principles for drug therapy*; Oxford University Press: New York. 334-336.
3. Auras R, Harte B, Selke S. (2004). An overview of Polylactides as Packaging Materials. *Macromol, Biosci*. 4: 835-864.
4. Ikada Y, Tsuj H. 2000. Biodegradable polyesters for medical and ecological applications. *Macromol. Rapid Commun*. 21:117-132.
5. Dorgan JR, Lehermeier HJ, Palade LI, Cicero J. (2001). Polylactide: Properties and Prospects of an Environmentally Benign Plastic from Renewable Resources.
6. Moon S, Taniguchi I, Miyamoto M, Kimura Y, Lee CW. (2001). Synthesis and Properties of High-Molecular-Weight Poly (L-Lactic Acid) by Melt/Solid Polycondensation under Different Reaction Conditions. *High Performance Polymers*. 13: 189-196.
7. Ran XH, Jia Z, Han C, Yang Y, Dong L. (2010). Thermal and Mechanical Properties of Blends of Polylactide and Poly(ethylene glycol-co-propylene glycol): Influence of

- Annealing. *Journal of Applied Polymer Science*. 116: 2050-2057.
8. Santos JMCA, Guthrie JT. (2005). Analysis of interactions in multicomponent polymeric systems: The key-role of inverse gas chromatography. *Mater Sci Eng R*. 50: 79-107.
 9. Gamelas JAF. (2013). The surface properties of cellulose and lignocellulosic materials assessed by inverse gas chromatography: a review. *Cellulose*. 20: 2675-2693.
 10. Mukhopadhyay P, Schreiber HP. (1995). Aspects of acid-base interactions and use of inverse gas chromatography. *Colloids Surf A*. 100: 47-71.
 11. Gamelas JAF, Ferraz E, Rocha F. (2014). An insight into the surface properties of calcined kaolinitic clays: The grinding effect. *Colloids Surf A*. 455: 49-57.
 12. Ansari DM, Price GJ. (2004). Chromatographic estimation of filler surface energies and correlation with photodegradation of kaolin filled polyethylene. 45: 1823-1831.
 13. Fekete E, Moczo J, Pukanszky B. (2004). Determination of the surface characteristics of particulate fillers by inverse gas chromatography at infinite dilution: a critical approach. *J Colloid Interface Sci*. 269: 143-152.
 14. Ward TC, Lloyd DR, Schreiber HP, Clara CP (Eds). (1989). *Inverse Gas Chromatography*, ACS Symp Publications. 391.
 15. Cline D, Dalby R. (2002). Predicting the Quality of Powders for Inhalation from Surface Energy and Area. *Pharm Res*. 19: 1274-1277.
 16. Feeley JC, York P, Sumbly BS, Dicks H. (2002). Processing effects on the surface properties of α -lactose monohydrate assessed by inverse gas chromatography (IGC). *Journal of Materials Science*. 37: 217-222.
 17. Ticehurst MD. (1995). Characterisation of the surface energetics of pharmaceutical powders by inverse gas chromatography. University of Bradford. York. Ph.D. thesis.
 18. Buckton G. (1997). Characterisation of small changes in the physical properties of powders of significance for dry powder inhaler formulations. *Adv Drug Delivery Rev*. 26: 17-27.
 19. Al-Ghamdi A, Al-Saigh ZY. (2002). Surface and thermodynamic characterization of conducting polymers by inverse gas chromatography. I. Polyaniline. *J Chromatogr A*. 69: 229-243.
 20. Que RWuD, Al-Saigh ZY. (2007). Surface and thermodynamic characterization of conducting polymers by inverse gas chromatography: II. Polyaniline and its blend. *J Chromatogr A*. 1146: 93-102.
 21. Boukerma K, Micusik M, Mravcakova M, Omastova M, Vaulay MJ., et al. (2007). Surfactant-assisted control of the surface energy and interfacial molecular interactions of polypyrrole. *Colloids Surf A*. 293: 28-38.
 22. Bailey RA, Persaud KC. (1998). Application of inverse gas chromatography to characterisation of a polypyrrole surface. *Anal Chim Acta*. 363: 147-156.
 23. Surana R, Randall L, Pyne A, Vemuri NM, Suryanarayanan R. (2003). Determination of glass transition temperature and in situ study of the plasticizing effect of water by inverse gas chromatography. *Pharm Res*. 20: 1647-1654.
 24. Shi B, Zhang Q, Jia L, Liu Y, Li B. (2007). Surface Lewis acid-base properties of polymers measured by inverse gas chromatography. *J Chromatogr A*. 1149: 390-393.
 25. Santos J, Gil H, Portugal A, Guthrie JT. (2001). Characterisation of the surface of a cellulosic multi-purpose office paper by inverse gas chromatography. *Cellulose*. 8: 217-224.
 26. Voelkel A, Grzeskowiak T. (2000). The use of solubility parameters in characterization of titanate modified silica gel by inverse gas chromatography. *Chromatographia*. 51: 608-614.
 27. Newell E, Buckton G, Butler DA, Thielmann F, Williams DR. (2001). The Use of Inverse Phase Gas Chromatography to Measure the Surface Energy of Crystalline, Amorphous, and Recently Milled Lactose. *Pharm Res*. 18: 662-666.
 28. Kalantzopoulou FR, Artemiacti T, Bassiotis I, Katsanos NA, Plagianakos V. (2001). Time separation of adsorption sites on heterogeneous surfaces by inverse gas chromatography. *Chromatographia*. 53: 315-320.
 29. Reutenauer F, Thielmann. (2003). The characterization of Cotton Fabrics and the Interaction with Perfume Molecules by Inverse Gas Chromatography (IGC). *J Mater Sci*. 38: 2205-2208.
 30. Chow AH, Tong HH, Shekunov BY, York P. (2004). Use of inverse gas chromatography (IGC) to determine the

- surface energy and surface area of powdered materials. *Pharma Res.* 21: 1718-1720.
31. Askin A, Yazici DT. (2008). A study of the surface analysis of some water-soluble polymers by inverse gas chromatography. *Surf Interface Anal.* 40:1237-1241.
32. Sreekanth TVM, Reddy KS. (2007). Analysis of Solvent-Solvent Interactions in Mixed Isosteric Solvents by Inverse Gas Chromatography. *Chromatographia.* 65: 326-330.
33. Yang YC, Yoon PR. (2007). Examination of the surface properties of kaolinites by inverse gas chromatography: Acid-base properties. *Korean J. Chem Eng.* 24: 451-456.
34. Przybyszewska M, Krzywania A, Zaborski M, Szyrkowska Ml. (2009). Surface properties of zinc oxide nanoparticles studied by inverse gas chromatography. *J Chromatogr A.* 1216: 5284-5291.
35. Hamieh T, Rageul-Lescouet M, Nardin M, Schultz J. (1996). Study of the surface properties of some metal oxides by reverse gas chromatography and by zetametry in aqueous and organic media. *J Chim Phys.* 93:1332-1363.
36. Hamieh T, Rageul-Lescouet M, Nardin M, Haidara H, Schultz J. (1997). Study of acid-base interactions between some metallic oxides and model organic molecules. *Colloids and Surfaces A: Phys. and Eng. Aspects.* 125: 155-161.
37. Hamieh T, Rezzaki M, Grohens Y, Schultz J. (1998). Glass transition of adsorbed stereoregular PMMA by inverse gas chromatography at infinite dilution. *J Chim Phys.* 95: 1964-1990.
38. Hamieh T, Rezzaki M, Schultz J. (2001). Study of the second order transitions and acid-base properties of polymers adsorbed on oxides, by using inverse gas chromatography at infinite dilution: I. Theory and Methods. *J Colloid and Interface Science.* 233: 339-342.
39. Hamieh T, Rezzaki M, Schultz J. (2001). Study of the second order transitions and acid-base properties of polymers adsorbed on oxides, by using inverse gas chromatography at infinite dilution: II Experimental results. *J Colloid and Interface Science.* 233: 343-347.
40. Hamieh T, Rezzaki M, Schultz J. (2001). Study of the transition temperatures and acid-base properties of poly (methyl methacrylate) adsorbed on alumina and silica, by using inverse gas chromatography technique. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 189: 279-291.
41. Hamieh T. (2011). Determination of the Transition Phenomena of Poly(α -n-alkyl) methacrylates Adsorbed on Silica by Inverse Gas Chromatography (IGC). *J Polym Res.* 18: 1159-1168.
42. Hamieh T. (2011). New Approach for the Determination of Acid-base Properties of Poly(α -n-alkyl) Methacrylates Adsorbed on Silica by Inverse Gas Chromatography (IGC). *Chromatographia.* 73: 709-719.
43. Hamieh T. (2011). Study of the Specific Entropy of Poly (α -n-alkyl) Methacrylates Adsorbed on Alumina or Silica by Inverse Gas Chromatography (IGC). *Soft Materials.* 9: 15-31.
44. Saint Flour C, Papirer E. (1982). Gas-solid chromatography. A method of measuring surface free energy characteristics of short glass fibers. 1. Through adsorption isotherms. *Ind Eng Chem Prod Res Dev.* 21: 337-341.
45. Saint Flour C, Papirer E. (1982). Gas-solid chromatography: method of measuring surface free energy characteristics of short fibers. 2. Through retention volumes measured near zero surface coverage. *Ind Eng Chem Prod Res Dev.* 21: 666-669.
46. Papirer E, Vidal A, Balard H. (1989). Analysis of solid surface modification. in *Inverse Gas Chromatography: Characterization of Polymers and Other Materials*, ACS Symposium Series 391, Lloyd DR, Ward TC and Schreiber ed, Washington. P: 248-261.
47. Hamieh T, Toufaily T, Mouneimne AB. (2011). Effect of the Tacticity of PMMA Adsorbed on Alumina and Silica on the Specific Entropy Change of Polymer by Inverse Gas Chromatography. *Chromatographia.* 73: 99-107.
48. Hamieh T, Schultz J. (2002). New approach to characterise physicochemical properties of solid substrates by inverse gas chromatography at infinite dilution. I. Some new methods to determine the surface areas of some molecules adsorbed on solid surfaces. *Journal of Chromatography A.* 969: 17-25.
49. Hamieh T, Fadlallah MB, Schultz J. (2002). New approach to characterise physicochemical properties of solid substrates by inverse gas chromatography at infinite

- dilution. III. Determination of the acid-base properties of some solid substrates (polymers, oxides and carbon fibres): a new model. *Journal of Chromatography A*. 969: 37-47.
50. Van Alsten JG, Sauer BB, Walsh J. (1992). Polymer dynamics at the melt/solid interface: experimental evidence of reduced center of mass mobility. *Macromolecules*. 25: 4046-4048.
51. Siffert B, Kuczinski J, Papirer E. (1990). Relationship between electrical charge and flocculation of heavy oil distillation residues in organic medium. *J Colloid Interface Sci*. 135: 107-117.
52. Schultz J, Lavielle L, Martin C. (1987). The role of the interface in carbon fibre-epoxy composites. *Journal of Adhesion*. 23: 45-60.
53. Ansari DM, Price GJ. (2004). Correlation of mechanical properties of clay filled polyamide mouldings with chromatographically measured surface energies. *Polymer*. 45: 3663-3670.
54. James AT, Martin JP. (1952). Gas-liquid partition chromatography: the separation and micro estimation of volatile fatty acids from formic acid to dodecanoic acid. *Biochem*. 50: 679-690.
55. Conder JR, Young CL. (1979). Physical measurements by gas chromatography. Eds: Wiley J and Sons. New York.
56. Gutmann V. (1978). The Donor-acceptor Approach to Molecular Interactions. Plenum. New York.
57. Riddle FL, Fowkes FM. (1990). Spectral shifts in acid-base chemistry. Van der Waals contributions to acceptor numbers, Spectral shifts in acid-base chemistry. 1. van der Waals contributions to acceptor numbers. *J Am Chem Soc*. 112: 3259-3264.
58. Hamieh T, Rageul-Lescouet M, Nardin M, Rezzaki M, Schultz J. (1997). Study of the specific interactions between certain metallic oxides and model organic molecules. *J Chim Phys*. 94: 503-521.