

New Methods for the Determination of the Surface Physicochemical Properties and Glass Transition of Polyaniline in Conducting and Non-Conducting Forms by Using Igc Technique at Infinite Dilution

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Abstract

Many studies were devoted in our Laboratory to the determination of physico-chemical and thermodynamic properties of polymers and/or oxides by using the inverse gas chromatography (IGC) at infinite dilution. More particularly, we studied the interactions of solid substrates with some model organic molecules and their acid-base properties, in Lewis terms, by determining the acidic and basic constants.

We proposed in this paper to study the surface thermodynamic energetics, transition phenomena, specific interactions and acid-base properties of both the conducting polyaniline (PANI-HEBSA) and the non-conducting form (PANI-EB) on the light of the new progresses of IGC methods. This technique was used to obtain the net retention volume V_n and then the dispersive free enthalpy of *n*-alkanes adsorbed on PANI. The curves of the dispersive component of the surface energy of *n*-alkanes adsorbed on PANI, as a function of the temperature highlighted the presence of two transition temperatures on 383 K and 430 K respectively for PANI-HEBSA and PANI-EB. These results were confirmed by the curves of $RT \ln V_n = f(1/T)$ of *n*-alkanes.

The determination of the specific free enthalpy ΔG_a^{SP} of polar molecules adsorbed on PANI proved a shift of 4 K in the value of the glass transition of PANI-EB. From the variation of ΔG_a^{SP} as a function of the temperature, one deduced the values of the specific enthalpy ΔH_a^{SP} of the various polar molecules and determined the acidic constant K_A and basic constant K_D , the two constants characterizing the solid substrate. It was showed that PANI is highly more basic than acidic (about 2.6 times more basic) and an increase of the acid-base character was highlighted near the glass transition for PANI-EB.

Keywords: Reagent stability • Plasma • Alzheimer's disease • Immunomagnetic reduction

Introduction

Polyaniline (PANI) has been widely studied due to its various useful properties as well as to its environmental stability [1]. Polyaniline is finding widespread use in novel organic electronic applications such as, light emitting diodes (LED), electroluminescence, metallic corrosion resistance, organic rechargeable batteries, biological and environmental sensors, composite structures, bioelectronics medical devices, and a variety of other applications where tunable conductivity in an organic polymer is desirable [2]. However, very few of the studies deal with the thermal behavior of the emeraldine salt form of PANI both as powder or film cast from solution [1]. Many researches were conducted on the thermal behavior of PANI-EB [1,3-5]. Many papers studied the thermal and mechanical properties of polyaniline doped or non-doped, in powder form or in films, by means of dynamic mechanical analysis, differential scanning calorimetry and thermogravimetric analysis [6-11].

Inverse gas chromatography was also used to characterize both doped, the undoped polyaniline (PANI), and its blend with nylon-6 using many

solutes. The change in the morphology of these polymers was detected in the temperature interval (80°C-180°C) including the study of the crystallinity [12].

Al-Saigh et al. [11] studied some surface thermodynamic characteristics, such as surface energy and other interaction properties of polyaniline in conducting and non-conducting forms by using inverse gas chromatography. They evaluated the interaction and dispersive force of polyaniline with alkyl acetates and alcohols. They observed for acetates and alcohols a maximum of around 145.8°C traducing a phase change from a semicrystalline to amorphous phase.

Data about the glass transition temperature (T_g) of EB are also scarce and rather controversial. By means of differential mechanical thermal analysis (DMTA) some authors have registered relaxations transitions in the chemically synthesized PANI-EB film cast from NMP solution [1]. Depending on the amount of the residual solvent in the film, T_g has been determined in the region 105°C -220°C. DMTA studies by Chen et al. [5] showed three relaxation transitions in PANI-EB films. According to them, the T_g of such films varied between 99 and 158 °C depending on the NMP content.

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Polyaniline doped by camphor sulphonic acid (PANI-CSA) exhibits a high electronic conductivity [13]. All the authors agree to invoke in various extents the role of disorder in the evolution of the transport properties as a function of temperature. The rigidity of the PANI chains was confirmed, in both a conducting and a partially doped sample. All the observable quasielastic scattering occurs from the CSA dynamics.

Ding et al. [14] highlighted the presence of two glass transitions T_g : 70°C and 250°C, in PANI-EB. Powder was observed for the first time using MDSC during the process of heat treatment. Later, Han et al. [15] studied the effect of solvent and dopant on the thermal transition of polyaniline (PANI) by using dynamic mechanical analysis (DMA) and found for the solvent N-methyl-2-pyrrolidinone (NMP) containing film three thermal transitions temperatures (142, 198, and 272°C). Rannou et al. [16] showed that diesters doped PANI exhibits two glass transition temperatures $T_{g1}=275$ K and $T_{g2}=304$ K corresponding to the freezing of the movement of the dopant substituents and of the movements of polymer-dopant anion association, whereas, with PANI-CSA, they proved a glass transition between 403 and 425 K.

In 2012, Farbod and Khajehpour Tadavani [17] proved that the glass transition temperature of the pure PANI was measured $T_g=378$ K using electrical resistivity measurement. The T_g increased up to 394 K when the PANI is doped up to 16 wt.% of functionalized multiwall carbon nanotubes (MWCNTs). The T_g of pure PANI was observed to be dependent on the pelletizing pressure and increased from 373 K to 387 K when the pelletizing pressure is increased from 96 to 1150 MPa.

The restricted molecular motions in rigid crystalline polymers like PANI are the essential cause of the extreme difficulty to the detection of its glass transition T_g . As a result, the reported T_g of PANI varies from -12°C to +250°C [18-21]. The reported literatures also show that the T_g of PANI depends remarkably on the processing temperature, heat treatment time, measurement techniques, type and concentration of dopant, solvent content, presence of chain ordering material, the molecular weight of the polymer, presence of plasticizers fillers and on the experimental techniques and conditions of measurement [18-20].

We were interested in this paper to the determination of dispersive surface energy interactions and acid-base properties of both doped polyaniline and the non-conducting form by using inverse gas chromatography technique at infinite dilution. Different IGC methods were used and compared each other to quantify the dispersive component of the surface energy of PANI as well as the specific interactions and the acid base constants in Lewi terms. Organic molecules such as n-alkanes molecules and polar organic were used in this study. The n-alkanes were used to determine the dispersive energy of polymers and the polar molecules served to determine the specific interactions between polyaniline and these probes. The retention time obtained by IGC technique was revealed an excellent experimental parameter to characterize the surface properties of the polymers.

Theory and Methods

Since 1982, many scientists used the inverse gas chromatography to determine surface phenomena, glass transitions and acid-base properties of solid materials [22-41]. The changes of the thermodynamic variables determined by IGC technique, as a function of temperature, of the surface properties of solid materials or nanomaterials, polymers, oxides or polymers adsorbed on oxides are considered now as powerful parameters to detect any evolution in the surface properties of materials. Model organic molecules of known properties are injected in the column containing the solid. One of the most important parameters is the retention time of injected molecules, measured at infinite dilution, allowing the determination of the interactions between the probes and the solid surfaces. The net retention volume was obtained from the experimental values of the retention time:

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

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 [42].

The free energy of adsorption ΔG^0 of n-alkanes on the solid surface was calculated from the following equation:

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

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 [43-48].

The dispersive component of the surface energy of PANI was calculated from Fowkes approach by using different models of the surface areas of the various molecules.

The Fowkes relation used the geometric mean of the respective dispersive components of the surface energy of the probe γ_1^d and the solid γ_s^d :

$$\Delta G^0 = \Delta G^d = NaWa = 2 Na (\gamma_1^d \gamma_s^d)^{1/2} \quad (3)$$

Where Wa is the energy of adhesion, N is Avogadro's number and a is the surface area of one adsorbed molecule of the probe.

For polar molecules, the specific interactions are added to the dispersive interactions:

$$\Delta G^0 = 2 Na (\gamma_1^d \gamma_s^d)^{1/2} + \Delta G^{sp} \quad (4)$$

By plotting $RT \ln V_n$ as a function of $2Na (\gamma_1^d)^{1/2}$ of n-alkanes, it is possible to deduce, from the slope of the straight line, the value of dispersive component γ_s^d of the surface energy of the solid. If γ_1^d , γ_s^d and a cross section of an adsorbed molecule, are known, it is possible to calculate the contribution to the free energy of adsorption of the Lewis acid-base surface interactions ΔG^{sp} by using equation (4) [49].

In previous studies, Hamieh et al. [50,51] proved the effect of the temperature on the surface area of n-alkanes and polar molecules and concluded to the non-validity of Fowkes method to be used for the determination of the dispersive surface energy and the specific free enthalpy of adsorption. They proposed various theoretical models giving the molecular areas of n-alkanes: geometrical model, cylindrical molecular model, liquid density model, BET method, Kiselev results and the two-dimensional Van der Waals and Redlich-Kwong models. These different models were used in the experimental section to compare between the obtained values of γ_s^d of the polymer.

On the other hand, the limitations of Fowkes method due, in part, to the fact that the molecular area a is not exactly known and varies both with the nature of the solid, and the temperature and surface coverage, led us to consider the method proposed Papier et al. [52,53].

Papier et al. method [43,44] obtained a straight line when plotting $RT \ln V_n$ against the logarithm of the vapor pressure P^0 on-alkanes. For a homologous series of n-alkanes:

$$RT \ln V_n = A \ln P_0 + B \quad (5)$$

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:

$$\Delta G^0 = \Delta G^d + \Delta G^{sp} \quad (6)$$

Where ΔG^{sp} refers to specific interactions of a polar molecule adsorbed

on solid substrate.

The Papirer method was used to determine the specific free energy of adsorption of polar molecules on PANI surfaces.

From the values of ΔG^{sp} of the polar molecules for different temperatures, the specific enthalpy

(ΔH^{sp}) and entropy ΔS^{sp} were deduced by using:

$$\Delta G^{sp} = \Delta H^{sp} - T \Delta S^{sp} \quad (7)$$

Knowing ΔH^{sp} of the various polar molecules, the acidic constant KA and basic constant KD, the two constants characterizing the solid substrate, are determined by using the following classical relationship:

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

Where DN and AN are the donor and acceptor numbers of electrons of the polar molecules.

This relation was corrected by Hamieh et al. [45,46,54,55] and proposed a new relationship by adding a third parameter K reflecting the amphoteric character of the oxide according to:

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

Experimental part

Materials and solvents: Polyaniline doped ethylbenzene sulfonic acid (PANI-EB) and the conducting form (PANI-HEBSA) was both obtained from Merck with a molecular mass of 50,000 in hexafluoroisopropanol (HFIP) to form a solution.

Organic molecules such as n-alkanes from C5 to C10 and polar molecules (alkyl acetates and alcohols) were used in this study. They are characterized by their donor and acceptor numbers [54-56]. On, we gave the donor and acceptor numbers of polar solvents.

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

Polar probes	DN'	AN'	DN'/AN'	Acid base character
MeOH	47.5	41.7	0.88	Amphoteric with higher basicity and acidity
EtOH	51.25	35.9	0.7	Amphoteric with high basicity and acidity
PrOH	52	34.4	0.66	Amphoteric with high basicity and acidity
BuOH	52.75	31.7	0.6	Amphoteric with high basicity and acidity
MeAc	41.25	5.7	0.14	Strong basicity
EtAc	42.75	5.3	0.12	Strong basicity
PrAc	44.5	4.9	0.11	Strong basicity
BuAc	47.5	4.2	0.09	Stronger basicity

GC conditions: The PANI powder was used with particle diameters ranging from 100 to 250 μ m. 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 300 g of polymer 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 carried out with a DELSI GC 121 FB Chromatograph equipped with a flame ionization detector of high sensitivity. Helium was used as carrier gas; its flowrate was equal to about 20 mL min⁻¹. IGC measurements at infinite dilution were done by varying the temperature from 40°C to 180°C. The IGC system has been used to make infinite dilution (ID) pulse experiments, probes were injected manually with a 1 μ L Hamilton syringe. The injection volume for each probe was 0.1 μ L, in order to approach linear condition gas chromatography. At least three injections were made for each probe and

the average retention time, $t_{R,i}$, was used for the calculations. The standard deviation was less than 1% in all measurements.

Results and Discussion

Determination of the dispersive surface energy of PANI

The dispersive component of the surface energy of PANI was calculated by using the various surface areas of n-alkanes using different models [46,47,50]. The obtained results show an important difference in the values of γ_s^d , however, they can be considered as qualitative rather than quantitative, more particularly to obtain a general tendency of the dispersive energy of polymers, and especially, for the determination of the glass transition.

We plotted the variations of $RT \ln V_n$ as a function of $2 N_A \sqrt{V_l^d}$ of n-alkanes at various temperatures and we deduce the values of γ_s^d of the two PANI forms for all used molecular models for different temperatures. On Figures 1 and 2, we presented the obtained curves of γ_s^d for all different surface area models. We showed that the linearity of $\gamma_s^d(T)$ is not satisfied. Two linear zones were highlighted. The corresponding straight lines intersected at a particular temperature for the two-studied PANI (in conducting and non-conducting forms). In case of PANI-HEBSA, the temperature is relative to a transition temperature about $T_{g1} = 383$ K (110°C) probably due to the surface modification of PANI-HEBSA or perhaps to the departure of some remaining water molecules in the column. For the doped PANI-EB, we obtained $T_{g2} = 430$ K (157°C). These results proved the dependency of the glass transition of PANI on the forms of added compounds. It seems that the doped non-conducting PANI form increases the value of the glass transition. IGC was able to detect these variations even when using the evolution of the dispersive surface energy of the polymer independently of the used models of the surface areas of the probes.

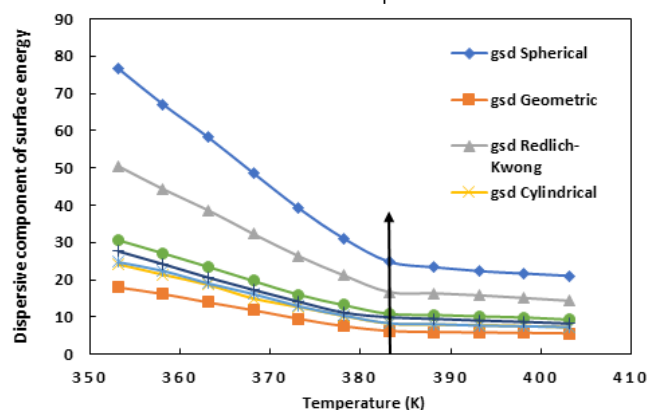


Figure 1. Variations of the dispersive component of the surface energy γ_{sd} (mJ/m²) of PANI-HEBSA as a function of the temperature T (K) for the various molecular area models.

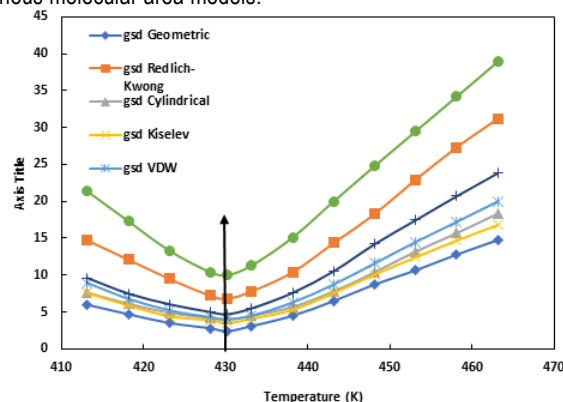


Figure 2. Variations of the dispersive component of the surface energy γ_s^d (mJ/m²) of PANI-EB as a function of the temperature T (K) for the various

molecular area models.

On Tables 2 and 3, we gave the various equations of the dispersive component of the surface energy γ_s^d of PANI in conducting and non-conducting forms versus the temperature T (K), the values of the slope ($d\gamma_s^d/dT$) (equivalent to the surface entropy) and the extrapolated values at 298 K and 0 K of the dispersive surface energy of the polymers. For PANI-HEBSA, we proved that the two zones relative to the two temperature

intervals are characterized by negative slope for all molecular area models varying from -0.41 to -1.76 mJ m⁻² K⁻¹ for the interval (353 K–383 K) and from -0.03 to -0.41 mJ m⁻² K⁻¹ for the interval (383 K–403 K) (Table 2). Whereas, in the case of PANI-EB, we obtained an inversion in the sign of the relative slope that became positive for the domain of temperature (430 K–463 K) (Table 3) proving an increase in the dispersive surface energy after the glass transition.

Table 2. Equations of dispersive component of the surface energy γ_s^d (mJ/m²) of PANI-HEBSA as a function of the temperature T (K) for two temperature intervals, values of the surface entropy and the extrapolated values at 298K and 0K of the dispersive surface energy.

Temperature interval T: 353 K – 383 K					
Model of surface area	Equation of γ_s^d (mJ/m ²)	R ²	$\frac{d\gamma_s^d}{dT}$ ($\frac{mJ}{m^2K}$)	Extrapolated $\gamma_s^d(298K)$	Extrapolated $\gamma_s^d(T = 0K)$
Geometric	$\gamma_s^d = -0.41 T + 160.9$	0.9961	-0.41	40.3	160.9
Redlich-Kwong	$\gamma_s^d = -1.14 T + 453.1$	0.9975	-1.14	112.9	453.1
Cylindrical	$\gamma_s^d = -0.54 T + 215.1$	0.9939	-0.54	53.8	215.1
Kiselev	$\gamma_s^d = -0.57 T + 224.4$	0.9962	-0.57	56.0	224.4
VDW	$\gamma_s^d = -0.68 T + 268.6$	0.9945	-0.68	67.5	268.6
Spherical	$\gamma_s^d = -1.76 T + 696.8$	0.9966	-1.76	172.7	696.8
Dorris-Gray	$\gamma_s^d = -0.61 T + 243.0$	0.9879	-0.61	60.8	243.0
Temperature interval T: 383 K – 403 K					
Geometric	$\gamma_s^d = -0.03 T + 17.6$	0.9418	-0.03	-	-
Redlich-Kwong	$\gamma_s^d = -0.12 T + 62.4$	0.9788	-0.12	-	-
Cylindrical	$\gamma_s^d = -0.047 T + 26.3$	0.9939	-0.047	-	-
Kiselev	$\gamma_s^d = -0.05 T + 28.8$	0.9903	-0.05	-	-
VDW	$\gamma_s^d = -0.08 T + 40.1$	0.9831	-0.08	-	-
Spherical	$\gamma_s^d = -0.19 T + 95.9$	0.9622	-0.19	-	-
Dorris-Gray	$\gamma_s^d = -0.42 T + 160.9$	0.9993	-0.42	-	-

Table 3. Equations of dispersive component of the surface energy γ_s^d (mJ/m²) of PANI-EB as a function of the temperature T (K) for two temperature intervals, values of the surface entropy and the extrapolated values at 298K and 0K of the dispersive surface energy.

Temperature interval T: 413 K – 430 K					
Model of surface area	Equation of γ_s^d (mJ/m ²)	R ²	$\frac{d\gamma_s^d}{dT}$ ($\frac{mJ}{m^2K}$)	Extrapolated $\gamma_s^d(298K)$	Extrapolated $\gamma_s^d(T = 0K)$
Geometric	$\gamma_s^d = -0.21 T + 91.5$	0.9883	-0.21	29.7	91.5
Redlich-Kwong	$\gamma_s^d = -0.48 T + 210.8$	0.9940	-0.48	69.2	210.8
Cylindrical	$\gamma_s^d = -0.54 T + 215.1$	0.9681	-0.21	31.7	94.8
Kiselev	$\gamma_s^d = -0.21 T + 94.8$	0.9598	-0.23	34.2	103.7
VDW	$\gamma_s^d = -0.29 T + 126.7$	0.9662	-0.29	41.5	126.7
Spherical	$\gamma_s^d = -0.68 T + 302.8$	0.9850	-0.68	99.5	302.8

Dorris-Gray	$r_s^d = -0.29 T + 126.4$	0.9723	-0.29	42.0	126.8
Temperature interval T: 430 K – 463 K					
Geometric	$r_s^d = 0.39 T - 163.4$	0.9953	0.39	-	-
Redlich-Kwong	$r_s^d = 0.77 T - 3245$	0.9905	0.77	-	-
Cylindrical	$r_s^d = 0.45 T - 190.4$	0.9823	0.45	-	-
Kiselev	$r_s^d = 0.42 T - 178.1$	0.9902	0.42	-	-
VDW	$r_s^d = 0.50 T - 213.1$	0.99	0.5	-	-
Spherical	$r_s^d = 0.90 T - 378.4$	0.9965	0.9	-	-
Dorris-Gray	$r_s^d = 0.60 T - 254.7$	0.9919	0.6	-	-

The important change in the slope of $r_s^d(T)$ for PANI in the different domains of temperature is attributed to a surface modification or to a relaxation of some surface groups of the polymer. This type of slope change was previously observed in other studies [57-59].

Variations of $RT\ln V_n=f(1/T)$ of n-alkanes adsorbed on PANI surfaces

The experimental results obtained with different n-alkanes adsorbed on PANI in both conducting and non-conducting forms confirmed those obtained with the dispersive component of the surface energy of the polymers. On Figures 3 and 4, we plotted the variations of $RT\ln V_n$ of n-alkanes from n-pentane C5 to n-decane C10 that clearly showed a transition temperature equal to 383 K for PANI-HSEBA and a glass transition for PANI-EB. Inverse gas chromatography can then highlight the presence of the transition phenomena in polymers more easily than the other techniques such as DSC or other calorimetric methods.

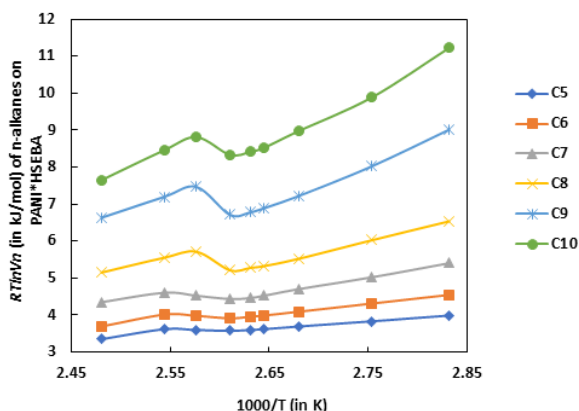


Figure 3. Variations of $RT\ln V_n$ (in kJ/mol) of n-alkanes adsorbed on PANI-HSEBA as a function of $1000/T$ (T in K)

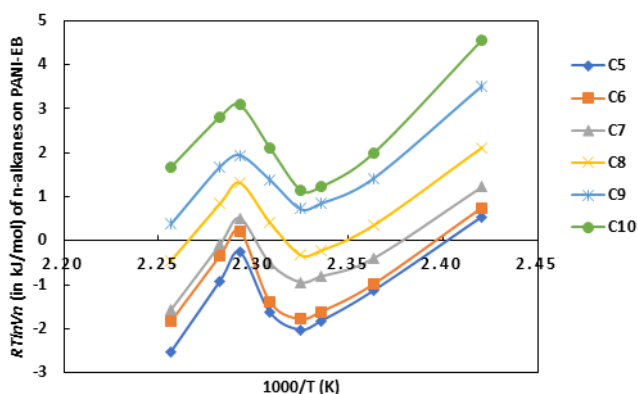


Figure 4. Variations of $RT\ln V_n$ (in kJ/mol) of n-alkanes adsorbed on PANI-EB as a function of $1000/T$ (T in K)

Determination of the specific interactions and acid-base constants of PANI

By using the experimental values relative to the retention times of n-alkanes and polar molecules adsorbed on PANI surfaces and equations (5) to (7). The results obtained with the conducting form of PANI-HEBSA are plotted on Figure 5 that gave the evolution of the specific free enthalpy of polar molecules on polymer surfaces.

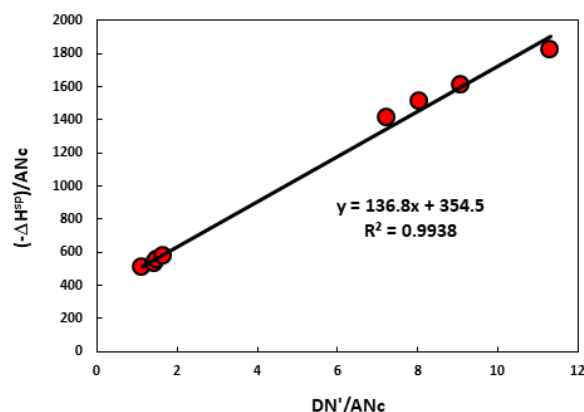


Figure 6. Variations of $-\Delta H^{sp} / ANc$ of different polar solvents adsorbed on PANI-HEBSA as a function of DN' / ANc

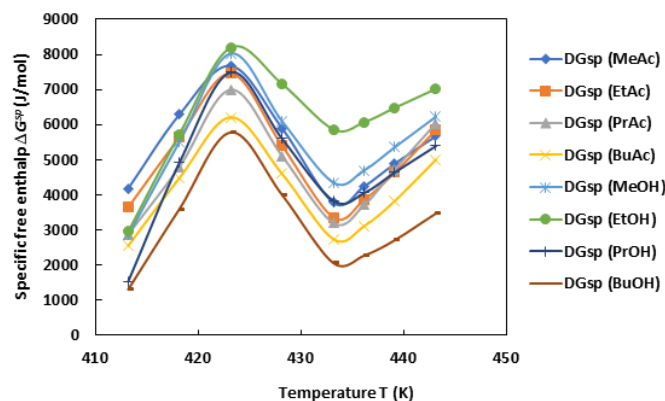


Figure 7. Curves of the specific free enthalpy of interaction of polar solvents adsorbed on PANI-EB as a function of the temperature.

The values of specific entropy $-\Delta S^{\text{sp}}$ and enthalpy $-\Delta H^{\text{sp}}$ of adsorption of the various polar probes are obtained by using the linearity of ΔG^{sp} (T) shown on Figure 5. The obtained values of $-\Delta H^{\text{sp}}$ of the different polar molecules allowed by using equation (8) and Table 1 were utilized to deduce the acid-base constants of the conducting polymer. On Figure 6, we gave the variations of $-\Delta H^{\text{sp}}/\text{ANc}$ of different polar solvents adsorbed on PANI-HEBSA as a function of DN'/ANc . Figure 6 showed that the alkyl acetate exchanged stronger interactions relative to the corresponding alcohols. This proved the strong basic character polyaniline and also the important amphoteric character because the alkyl acetates behave an important amphoteric character. Figure 6 allowed to deduce the acid and base constants in Lewis terms of PANI-HEBSA.

$$\begin{cases} K_A = 137 \\ K_D = 355 \end{cases} \quad \text{or} \quad \begin{cases} K_A = 0.082 \\ K_D = 0.212 \end{cases}$$

With the ratio of basic constant on acidic constant equal to $K_D/K_A = 2.6$. This proved that PANI is 2.6 times more basic than acidic.

Now, for the doped PANI-EB, the results are more complicated because of the presence of the glass transition at 430 K. The representation of the evolution of the specific free enthalpy of interaction (Figure 7) of polar molecules adsorbed on PANI-EB in the temperature interval (413.15 K, 443.15 K) as a function of the temperature again proved the transition temperature around 434 K (curves with Z-form) with a shift of 4 K in the case of polar molecules.

The acid-base properties of the used polymers in this case then depend on the temperature. Three zones were distinguished: (413.15 K, 423.15 K), (423.15 K, 433.15 K) and (433.15 K, 443.15 K). The corresponding values of the acid base constants of PANI-EB and those of PANI-HEBSA are given in Table 4 for the different domains of the temperature.

The strong basic character of PANI is shown in Table 4. Near the glass transition, we proved an increase of the basic and acidic character of PANI-EB with $K_D = 4.091$ and $K_A = 1.479$ with a ratio $K_D/K_A = 2.77$ close to that of PANI-HEBSA (Table 4). Figure 8 showed the variation of the acid base constants as a function of the temperature. Figure 8 clearly showed the decrease of acid-base constants of PANI when passing from the conducting form to non-conducting PANI but an important increase of the acid base character near the glass transition.

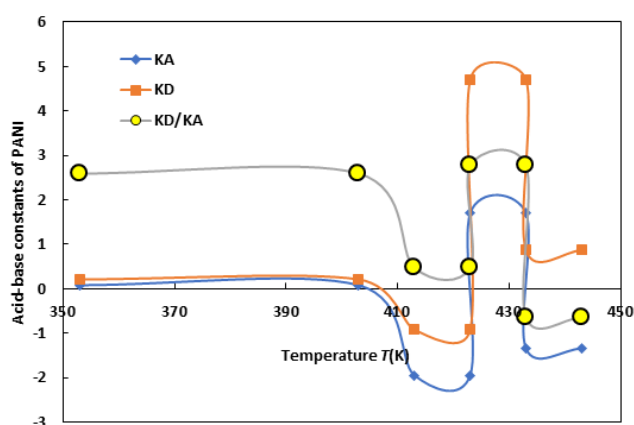


Figure 8. Curves of the specific free enthalpy of interaction of polar solvents adsorbed on PANI-EB as a function of the temperature

Conclusion

In this study, we determined the dispersive component of the surface energy, the specific interactions and the acid base constants of polyaniline in both conducting and non-conducting forms. Two transition temperatures were highlighted, the first one probably due to the modification of the surface

of PANI-HEBSA at a temperature $T_{g_1} = 383$ K and the second one relative to the glass transition of PANI-EB given by $T_{g_2} = 430$ K. The evolution of the dispersive energy of polymers showed these two temperatures for n-alkanes used in this study (C5 to C10). The evolution of the specific free enthalpy of interaction between the polymer and the polar molecules as a function of the temperature confirmed the shift of the glass transition for the adsorbed polar solvents on PANI-EB. Our results giving the values of the acidic and basic constants of different polymers, showed an important basic character of PANI. However, an increase of the acid-base force was highlighted for PANI-EB near the glass transition.

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There is no conflict of interests.

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