

Special Article: Acrylic Fibers

Determination of the Surface Thermodynamic Properties of Glass Textiles by Inverse Gas Chromatography at Infinite Dilution

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Received: July 25, 2023**Accepted:** September 06, 2023**Published:** September 13, 2023**Abstract**

Inverse gas chromatography at infinite dilution was used to determine the London dispersive surface energy of glass textiles. The free surface energy, the free specific energy, the enthalpy and entropy of adsorption of organic molecules on the glass fibers were determined. The Lewis's acid-base constants of glass textiles were calculated by using the various methods and models of the inverse gas chromatography as well as the different molecular models. The model giving the more accurate results is thermal model that took into account the effect of the temperature on the polar and non-polar molecules. It was proved that the glass textiles exhibited an amphoteric character with a surface about four times more basic than acidic. The pretreatment of glass fibers was proved to have an important effect on their surface properties. Indeed, in this case, the basic character decreased, while the acidic constant remained approximately identical to non-pretreated glass textiles.

Keywords: London dispersive surface energy; Specific surface enthalpy and entropy; Dispersive and specific adsorption; Lewis's acid base constants; Hamieh model

Introduction

It is well-known that the glass textiles are very used in many industrial applications, and especially, in high-performance reinforced composites [1-10]. In order to prevent the collapse of buildings and infrastructures, many materials were synthesized and produced with high performance mechanical composite properties. Many scientists were interested to high-performance materials, such as fiber-reinforced cementitious composites, high-performance fiber-reinforced concrete, cementitious composites and textile reinforced cementitious composites [1-5]. The textile reinforcements were used for the reinforcement efficiency of high-performance materials [2,6-10].

The glass textiles are one of the most widely employed reinforcement for the production of composite materials [10]. The glass reinforced polymers represents about 95% of the total production of reinforced polymers, and they are used in many industrial applications in the form of continuous filament woven in textiles or meshes, or as short fibers dispersed in the matrix. An important success of glass fiber as reinforcement of polymers was observed in the development of manufacturing processes and technological instruments for their production with a wide scientific literature [10]. The modification of fiber surface was widely studied for many technological applications [11-13], and especially, in cement-based composites such as

textile reinforced concrete and fabric reinforced cementitious matrix systems. The surface modifications are in general introduced to improve the stress transfer between the fibers to satisfy some required physicochemical properties.

The fiber glass reinforced composites can be found in many industrial fields from very specific applications to consumer applications. Some of these applications include: public works and building, electricity and electronics, sports, transportation, military sectors and energy generation devices [14].

Glass fibers are often used with thermosetting resins, in particular with epoxy resins. One of the applications of this type of composite concerns electronic device support plates [15] generally consisting of several layers of fine glass textiles pre-impregnated with brominated epoxy resin.

The surface physicochemical properties of the glass textiles can be advantageously determined by Inverse Gas Chromatography (IGC) at infinite dilution that was proved to be the best surface technique that allows to obtain the London dispersive energy, the free enthalpy of adsorption, the specific thermodynamic variables of adsorption of organic molecules on the solid surfaces as well as their Lewis acid-base parameters [16-30].

The aim of this paper is to study the stripped thermally glass textiles by using the IGC technique at infinite dilution. Two chromatographic columns were prepared with these glass textiles, the first one was used without pretreatment, whereas, the second one was pretreated at 150°C, over 15 hours. The glass fibers are characterized by a filament diameter of 9 mm, a thickness of 180 mm, a number of filaments in each filament yarn equal to 400 filaments and a surface mass of 200 g/m².

Methods

The surface thermodynamic properties of solid surfaces such as metals, oxides, textiles, polymers adsorbed on oxides and supported catalysts, were very determined by many scientists by IGC technique at infinite dilution [23-25,31-40]. Some corrections were introduced in literature to give more accurate values of the dispersive surface energy and Lewis's acid-base constants [34-37]. Due to their importance in many industrial processes and applications, one proposed to study the surface properties of glass textiles. We used different methods and models to characterize these glass fibres.

The important parameter highlighted by IGC technique is the net retention volume V_n of the organic solvents adsorbed on the solid surfaces. This parameter is a strong characteristic of the interaction between the studied materials and the probes injected in the chromatographic column. These probes can be polar or non-polar organic molecules. The non-polar such as n-alkanes characterize the dispersive properties of the solid materials, whereas, the polar solvents such as acetone, ethyl acetate, ethyl oxide, toluene, carbon tetrachloride, chloroform and dichloromethane.

In a previous paper [36], we showed the linear dependency of the net retention correlated V_n obtained from IGC technique, with respect of any thermodynamic parameters X_j of organic molecules. The general equation can be written as:

$$RT \ln V_n = a_i X_j + b_i, i \neq j \quad (1)$$

where R is the ideal gas constant, T the absolute temperature, and a_i and b_i are constants depending on the interaction between the solid surface and the organic solvents.

Sawyer and Brookman [17] used the notion of the boiling point $T_{B.P.}$ of the solvents, whereas, Saint-Flour and Papirer [18,19] related $RT \ln V_n$ to $\ln P_0$, where is the vapor pressure P_0 of the probes at a fixed temperature. Where R is the ideal gas constant, T the absolute temperature, a_2 and b_2 constants of interaction.

On the other hand, Schultz et al. [20] used the Fowkes's relation [22] and proposed the dispersive component γ_1^d of the surface energy of the solvent as a thermodynamic parameter correlated to $RT \ln V_n$ with the help of the surface area a of the probe supposed constant for all temperatures.

Later, Donnet et al. [23] proposed a method based on the deformation polarizability α_0 , whereas, Chehimi et al. [39,40] used the standard enthalpy of vaporization ΔH_{vap}^0 (supposed constant) of organic molecules. Brendlé and Papirer [24,25] used the concept of the topological index χ_T that is a parameter considering the topology and the local electronic density in the polar probe structure.

Now, by using one of the previous IGC methods, it is possible to determine the specific free energy ΔG_a^{sp} of adsorption of polar molecule on the solid substrate from the distance relat-

ing the representative point of $RT \ln V_n$ of a polar molecule to its hypothetical point located on the n-alkane straight-line. The specific enthalpy ΔH_a^{sp} and entropy ΔS_a^{sp} of the adsorbed polar molecule can be determined from the variation of $\Delta G_a^{sp}(T)$ versus the temperature:

$$\Delta G_a^{sp}(T) = \Delta H_a^{sp} - T \Delta S_a^{sp} \quad (2)$$

Knowing of ΔH_a^{sp} polar solvents, the two respective acid base constants K_A and K_D of solids can be determined by Papirer following relation [18,19]:

$$\frac{-\Delta H^{sp}}{AN} = \frac{DN}{AN} K_A + K_D \quad (3)$$

Where AN and DN respectively represent the electron donor and acceptor numbers of the polar molecule given by Gutmann [26] and corrected by Fowkes.

Furthermore, the dispersive component γ_s^d of the surface energy of the solid can be obtained by applying the method of Dorris and Gray [38] who first determined γ_s^d of solid materials by using Fowkes's relation [22] and the work of adhesion W_a to the free energy of adsorption ΔG_a^0 by the following relation:

$$\Delta G_a^0 = N a W_a = 2 N a \sqrt{\gamma_1^d \gamma_s^d} \quad (4)$$

Where N is the Avogadro's number.

Dorris and Gray introduced the increment $\Delta G_{-CH_2-}^0$ of two consecutive n-alkanes $C_n H_{2(n+1)}$ and $C_{n+1} H_{2(n+2)}$:

$$\Delta G_{-CH_2-}^0 = \Delta G^0(C_{n+1} H_{2(n+2)}) - \Delta G^0(C_n H_{2(n+1)}) \quad (5)$$

They supposed the surface area of methylene group, $a_{-CH_2-} = 6 \text{ \AA}^2$, independent from the temperature and the surface energy γ_{-CH_2-} (in mJ/m²) of $-CH_2-$ equal to:

$$\gamma_{-CH_2-} = 52.603 - 0.058 T \quad (T \text{ in K})$$

Dorris and Gray [38] then deduced the value of γ_s^d by the equation (6):

$$\gamma_s^d = \frac{\left[RT \ln \left[\frac{V_n(C_{n+1} H_{2(n+2)})}{V_n(C_n H_{2(n+1)})} \right] \right]^2}{4 N^2 a_{-CH_2-}^2 \gamma_{-CH_2-}} \quad (6)$$

Another method allowing to obtain γ_s^d of solid surfaces was proposed by Schultz et al. [20]

Molecular and Hamieh Thermal Models

In previous studies, one proposed the various molecular areas of Kiselev, Van der Waals (VDW), Redlich-Kwong (R-K), Kiselev, geometric, cylindrical or spherical models [28-30] to determine the dispersive component of many solid materials and the corresponding specific parameters. One also proved [34-37] that the method of Schultz et al. [20] cannot be used to characterize the solid surfaces and obtain quantitative properties, because they supposed the surface area of probes as constant and independent from the temperature. While, it was proved that the surface area of molecules is function of the temperature [34-37]. Consequently, the values of γ_s^d , ΔG_a^{sp} and the Lewis acid base parameters obtained many authors are definitely inaccurate and they have to be corrected. Indeed, one gave the different relations of the surface area $a(T)$ of organic molecules and n-alkanes versus the temperature and the surface area of methylene group $a_{-CH_2-}(T)$ also proving the non-validity of γ_s^d determined by Dorris-Gray relation [38].

We determined the surface properties of the glass textiles by applying the different IGC methods and the molecular models of the surface areas of molecules as well as the thermal model

taking into account the variations of the surface areas of organic molecules as a function of the temperature.

Experimental

Materials and Solvents

All chemicals used in this study such as the n-alkanes (pentane, hexane, heptane, octane, nonane), and the polar solvents (acid (CCl_4), strong acid probes (chloroform (CHCl_3) and Dichloromethane (DCM)), amphoteric solvent (toluene and acetone) and strong basic solvents (ethyl acetate, diethyl ether and Tetrahydrofuran (THF)) at highly pure grade (99%), were purchased from Fisher Scientific. The above polar organic probes are characterized by their donor and acceptor numbers. The corrected acceptor number and normalized donor number were used in this study and given in Table 1.

GC Conditions

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

Polar probe	DN'	AN'	DN'/AN'	Character
CCl_4	0	2.3	0	Acid
CHCl_3	0	18.7	0.00	Higher acidity
CH_2Cl_2	3	13.5	0.22	Acid
Toluene	9.75	3.3	2.96	Amphoteric
Acetone	42.5	8.7	4.89	Higher amphoteric
Ethyl acetate	42.75	5.3	8.07	Base
Diethyl ether	48	4.9	9.80	Base
THF	50	1.9	26.32	Higher basicity

Table 2: Equations $\gamma_s^d(T)$ of glass textiles (pretreated (I) and without pretreatment (II)) for the various molecular models of n-alkanes, ϵ_s^d , $\gamma_s^d(T = 0K)$ and T_{Max} .

Glass textiles I				
Molecular model	$\gamma_s^d(T)$ (mJ/m^2)	$\epsilon_s^d = d\gamma_s^d/dT$ ($\text{mJ m}^{-2}\text{K}^{-1}$)	$\gamma_s^d(T = 0K)$ (mJ/m^2)	T_{Max} (K)
Kiselev	$\gamma_s^d(T) = -0.20T + 97.3$	-0.20	97.3	479.4
Cylindrical	$\gamma_s^d(T) = -0.17T + 87.7$	-0.17	87.7	505.7
VDW	$\gamma_s^d(T) = -0.21T + 99.8$	-0.21	99.8	481.2
Geometric	$\gamma_s^d(T) = -0.11T + 59.6$	-0.11	59.6	545.5
Redlich-Kwong	$\gamma_s^d(T) = -0.34T + 163.0$	-0.34	163.0	481.2
Spherical	$\gamma_s^d(T) = -0.68T + 307.5$	-0.67	307.5	456.2
Hamieh	$\gamma_s^d(T) = -0.37T + 168.4$	-0.37	168.4	450.4
Dorris-Gray	$\gamma_s^d(T) = -0.15T + 84.8$	-0.15	84.8	556.4
Gray-Hamieh	$\gamma_s^d(T) = -0.51T + 229.4$	-0.51	229.4	445.6
Global average	$\gamma_s^d(T) = -0.31T + 144.2$	-0.31	144.2	472.3
Glass textiles II				
Molecular model	$\gamma_s^d(T)$ (mJ/m^2)	$\epsilon_s^d = d\gamma_s^d/dT$ ($\text{mJ m}^{-2}\text{K}^{-1}$)	$\gamma_s^d(T = 0K)$ (mJ/m^2)	T_{Max} (K)
Kiselev	$\gamma_s^d(T) = -0.17T + 81.1$	-0.17	81.1	484.3
Cylindrical	$\gamma_s^d(T) = -0.15T + 76.38$	-0.15	76.3	499.7
VDW	$\gamma_s^d(T) = -0.18T + 86.0$	-0.18	86.0	478.3
Geometric	$\gamma_s^d(T) = -0.10T + 52.1$	-0.10	52.1	535.8
Redlich-Kwong	$\gamma_s^d(T) = -0.29T + 140.5$	-0.29	140.5	478.2
Spherical	$\gamma_s^d(T) = -0.58T + 265.4$	-0.58	265.4	453.8
Hamieh a(T)	$\gamma_s^d(T) = -0.34T + 149.1$	-0.34	149.1	440.6
Dorris-Gray	$\gamma_s^d(T) = -0.13T + 72.6$	-0.13	72.6	555.4
Hamieh-Gray	$\gamma_s^d(T) = -0.45T + 198.6$	-0.45	198.6	443.6
Global average	$\gamma_s^d(T) = -0.27T + 124.6$	-0.27	124.6	468.8

Table 3: Variations of ($-\Delta H_a^{sp}$ in kJ mol^{-1}) as a function of the used models or methods of polar molecules respectively adsorbed on Glass textiles I and II.

Glass textiles I								
Probes	CCl_4	CH_2Cl_2	CHCl_3	Toluene	Ether	THF	EA	Acetone
Kiselev	-3.76	-0.62	40.26	-3.06	-19.05	2.90	2.68	5.09
Cylindrical	-4.22	-13.90	13.20	0.76	-26.82	2.60	3.96	3.35
VDW	4.82	3.68	-26.35	10.91	14.79	12.03	5.58	7.62
Geometric	12.75	11.18	-2.73	5.54	11.75	5.76	8.10	3.43
Redlich-Kwong	4.90	3.82	-29.86	10.91	14.86	12.11	5.59	7.61
Spherical	6.11	6.01	-39.77	13.10	16.28	12.61	6.35	9.43
Hamieh	6.07	23.70	68.13	18.53	36.72	42.42	27.61	32.36
Boiling point	4.19	-1.56	-0.07	1.10	-13.38	1.85	3.71	3.11
Vapor pressure	13.40	14.67	7.66	13.00	0.85	6.16	9.15	14.82
Deformation polarizability	14.40	-3.56	8.77	5.42	16.69	16.26	10.11	13.43
DH_{vap}	2.57	2.33	1.96	0.21	6.10	2.59	2.28	4.83
$DH_{vap}(T)$	10.10	4.16	16.12	6.18	25.10	16.90	-	-
Topological index	9.71	14.75	15.20	5.00	17.31	4.29	4.06	7.00
Average values	6.23	4.97	5.58	6.74	7.78	10.65	7.43	9.34
Glass textiles II								
Probes	CCl_4	CH_2Cl_2	CHCl_3	Toluene	Ether	THF	EA	Acetone
Kiselev	5.35	33.57	49.61	0.44	9.96	7.45	9.36	5.09
Cylindrical	1.64	8.99	34.12	0.57	16.48	5.74	4.01	7.41
VDW	1.03	29.12	35.98	-10.34	10.15	-2.05	6.30	6.75
Geometric	-10.80	2.80	7.33	-5.30	10.07	1.42	-6.82	0.92
Redlich-Kwong	0.97	29.60	39.12	-10.34	9.89	-26.44	2.43	6.78
Spherical	-0.25	36.43	52.24	-12.42	24.02	-10.94	5.19	4.66
Hamieh	6.95	70.27	68.19	18.03	36.41	42.25	26.98	32.73
Boiling point	4.09	-6.89	4.21	0.56	-0.29	1.45	3.49	4.25
Vapor pressure	0.46	1.96	2.09	6.04	10.03	1.30	11.50	9.52
Deformation polarizability	7.37	1.17	2.76	3.96	7.53	14.83	13.41	1.41
DHvap	3.54	2.00	3.50	1.61	1.01	2.52	0.27	2.29
DHvap(T)	14.67	12.83	15.94	14.68	27.07	21.55		
Topological index	11.32	18.71	12.00	5.27	23.80	12.62	5.79	9.02
Average values	3.56	18.50	25.16	0.98	14.32	5.52	6.83	7.57

Table 4: Variations of ($-\Delta S_a^{sp}$ in $J K^{-1} mol^{-1}$) as a function of the used models or methods of polar molecules respectively adsorbed on Glass textiles I and II.

Glass textiles I								
Probes	CCl ₄	CH ₂ Cl ₂	CHCl ₃	Toluene	Ether	THF	EA	Acetone
Kiselev	-10	7	137	-11	-33	37	17	35
Cylindrical	-9	-22	64	-3	-60	33	0	0
VDW	11	-1	-101	25	23	2	5	5
Geometric	24	17	-31	13	17	-12	3	-8
Redlich-Kwong	12	-1	-113	25	23	2	5	5
Spherical	15	3	-145	32	26	4	9	12
Hamieh	11	65	183	1	0	43	-18	8
Boiling point	15	3	4	6	-21	38	43	40
Vapor pressure	44	48	37	45	24	51	65	76
Deformation polarizability	20	9	12	4	27	3	-11	-9
DH _{vap}	11	9	0	5	0	39	35	42
DH _{vap} (T)	31	12	46	15	61	25		
Topological index	8	19	20	3	32	-28	-25	-24
Average values	14	13	9	12	9	18	11	15
Glass textiles II								
Probes	CCl ₄	CH ₂ Cl ₂	CHCl ₃	Toluene	Ether	THF	EA	Acetone
Kiselev	19	116	171	0	58	51	39	35
Cylindrical	9	48	131	3	71	43	26	35
VDW	7	105	136	-24	56	29	34	41
Geometric	-20	26	46	-12	51	35	2	23
Redlich-Kwong	7	107	146	-24	55	-44	22	41
Spherical	3	132	190	-30	99	1	29	33
Hamieh	34	248	229	67	141	173	124	139
Boiling point	14	-10	12	5	19	36	42	43
Vapor pressure	12	25	12	6	24	33	43	35
Deformation polarizability	15	1	0	4	25	-21	-23	-22
DH _{vap}	13	0	11	0	22	38	29	34
DH _{vap} (T)	46	35	53	43	69	41		
Topological index	15	28	17	4	52	0	-19	-16
Average values	12	66	89	3	56	32	29	35

Tables 5: Values of K_A , K_D , ω_A and ω_D of the two glass fibers I and II with the acid base ratios by using Hamieh thermal model.

Solid surface	K_A	K_D	K_A/K_D	$10^{-3}\omega_A$	$10^{-3}\omega_D$	ω_D/ω_A
Glass textiles I	0.43	1.08	2.49	0.34	0.73	2.15
Glass textiles II	0.41	1.52	3.76	1.68	5.79	3.44

The experimental measurements were performed on a commercial Focus GC 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 420 K during the experiments. To achieve infinite dilution, 0.1 μ L of each probe vapor was injected with 1 μ L Hamilton syringes, in order to approach linear condition gas chromatography. The two columns used in this study were prepared using a stainless-steel column with a 2 mm inner diameter and with an approximate length of 20 cm. The

column was packed with 1 g of solids in powder forms. The column temperatures were between 290 K and 360 K. 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.

Results

Determination of the Dispersive Surface Energy

The dispersive components of the surface energy of the glass textiles (non-pretreated and treated) were calculated by using the various molecular models, Dorris-Gray method and the thermal model [34-37] taking into account the variations of the surface area versus the temperature. The results were plotted on Figure 1. The variations of $\gamma_s^d(T)$ of the glass fibers as a function of the temperature showed linear variations with excellent correlation coefficient. One observed on Figure 1 a large difference between the values of $\gamma_s^d(T)$ calculating by the different models that can reach 100% in some cases. The more accurate results were obtained by the thermal model [34-37]. Figure 1 also showed that Redlich-Kwong model, cylindrical model and the average values gave the closer results relative to the thermal model, followed by Kiselev, Dorris-Gray and Hamieh-Gray models. The hypothesis of the classic methods of Schultz and Dorris-Gray considering the surface areas of organic molecules as constant independent from the temperature was proved to be wrong. On the other hand, one observed that the dispersive surface energy decreased for the pretreated glass textiles about 10mJ/m² as a function of the temperature. This is due certainly to the elimination of water molecules by thermal treatment of the glass fibers.

In order to understand the differences between the various molecular models for the two glass textiles, Table 2 presented the equations of $\gamma_s^d(T)$ determined for the glass fibers as a function of the temperature, the dispersive surface entropy ϵ_s^d , the extrapolated values $\gamma_s^d(T = 0K)$ and the maximum of temperature T_{Max} defined by: $T_{Max} = -\frac{\gamma_s^d(T=0K)}{\epsilon_s^d}$ for the two previous textiles.

The obtained equations on Table 2 proved that the results of Redlich-Kwong model are closer to that of Hamieh model once proving the strong effect of the temperature on the surface areas of molecules and therefore on the dispersive surface energy of materials. The maximum of temperature T_{Max} of the two glass fibers I and II are very closed $T_{Max} \approx 450K$.

The obtained values of the dispersive surface entropy ϵ_s^d and the extrapolated values $\gamma_s^d(T = 0K)$ varied from model to another model proving the non-validity of Schultz et al. method [20].

Specific Free Variables and Lewis's Acid-Base Parameters

By using the different molecular models and IGC methods, one determined the values of the specific variables such as the specific free energy ($\Delta G_a^{sp}(T)$) of polar solvents adsorbed on glass fibers as a function of the temperature (Tables SI1 and SI2) showing linear variations of ($\Delta G_a^{sp}(T)$) and irregular values between the different IGC methods and models as it can be shown on Figures 2. One presented on Figures 2 the evolution of ($\Delta G_a^{sp}(T)$) of CHCl₃, acetone and THF, whereas Figures (SI1) gave the variations of the specific free energy of CCl₄, CH₂Cl₂, toluene, diethyl ether and ethyl acetate.

The values obtained with different models and methods are not similar, they can vary from simple to double or triple as it is

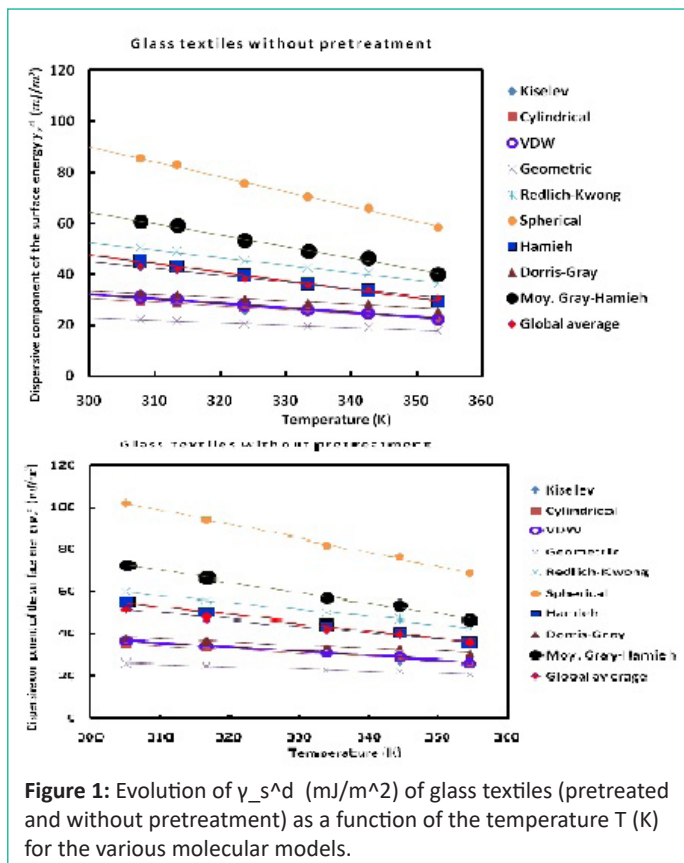


Figure 1: Evolution of γ_s^d (mJ/m²) of glass textiles (pretreated and without pretreatment) as a function of the temperature T (K) for the various molecular models.

shown in Figures 2 and S11. All these observations required the necessity to the correction of the classical methods and therefore using the new thermal model that considered the effect of the temperature on the surface area of the solvents.

The curves of Figures 2 clearly showed the importance difference the pretreated and non-pretreated glass textiles. Indeed, one observed for all polar molecules that the non-pretreated glass fibers exhibited larger values of the specific free energy of adsorption for all temperatures proving that the presence of water molecules effectively affects the glass fibers by dissociating their surface sites and inducing more important specific interactions between textile surfaces and the polar molecules.

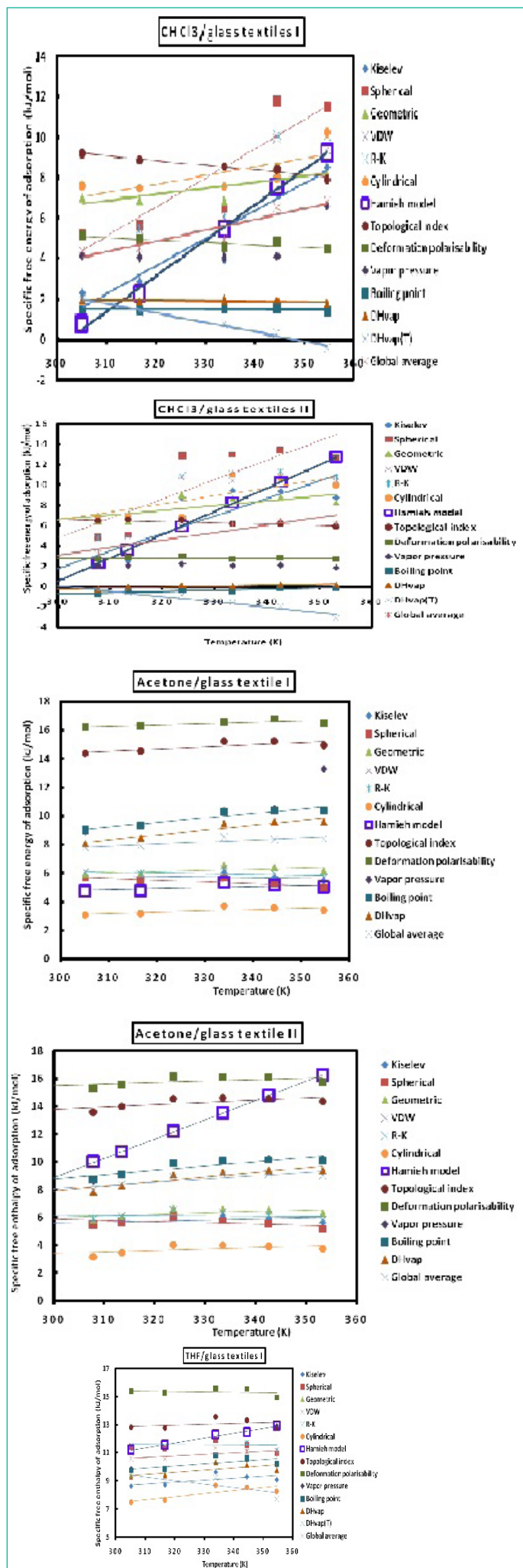
From the variations of $\Delta G_a^{sp}(T)$, one determined the specific enthalpy and entropy of polar molecules adsorbed on the glass textiles by using relation (2).

Enthalpic and Entropic Acid Base Constants

On Tables 3 and 4, one gave the values of $(-\Delta H_a^{sp})$ and $(-\Delta S_a^{sp})$ of polar molecules adsorbed on the glass fibers by using the various models and methods. Results obtained also showed irregular values of $(-\Delta H_a^{sp})$ and $(-\Delta S_a^{sp})$. Only the thermal model gave more accurate results because it took into account the thermal effect of the temperature on the surface area. One found a large difference between the two glass fibers. The specific variables values are more important for the non-pretreated glass textiles and especially for the interaction with the more acidic solvent such as CH₂Cl₂.

To determine the Lewis acid base constants of the glass fibers one represented the variations of $(\frac{-\Delta H_a^{sp}}{\Delta N^*})$ (Figure 3) and $(\frac{-\Delta S_a^{sp}}{\Delta N^*})$ (Figure S12) as a function of $(\frac{\Delta N^*}{\Delta N^*})$ for the different methods and models.

The linearity of the curves on Figures 3 and S12 is in general not insured for several of the applied models and methods. One determined the values of the acid base constants K_A, K_D, ω_A



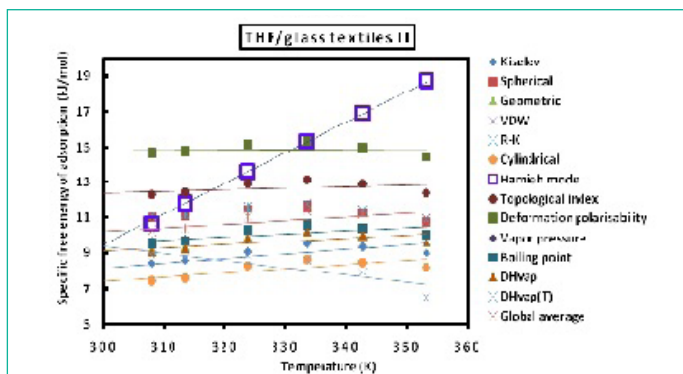


Figure 2: Variations of ΔG_a^{SP} of the various solvents (CHCl_3 , acetone and THF) adsorbed on glass textiles I and II as a function of the temperature for the different models and methods.

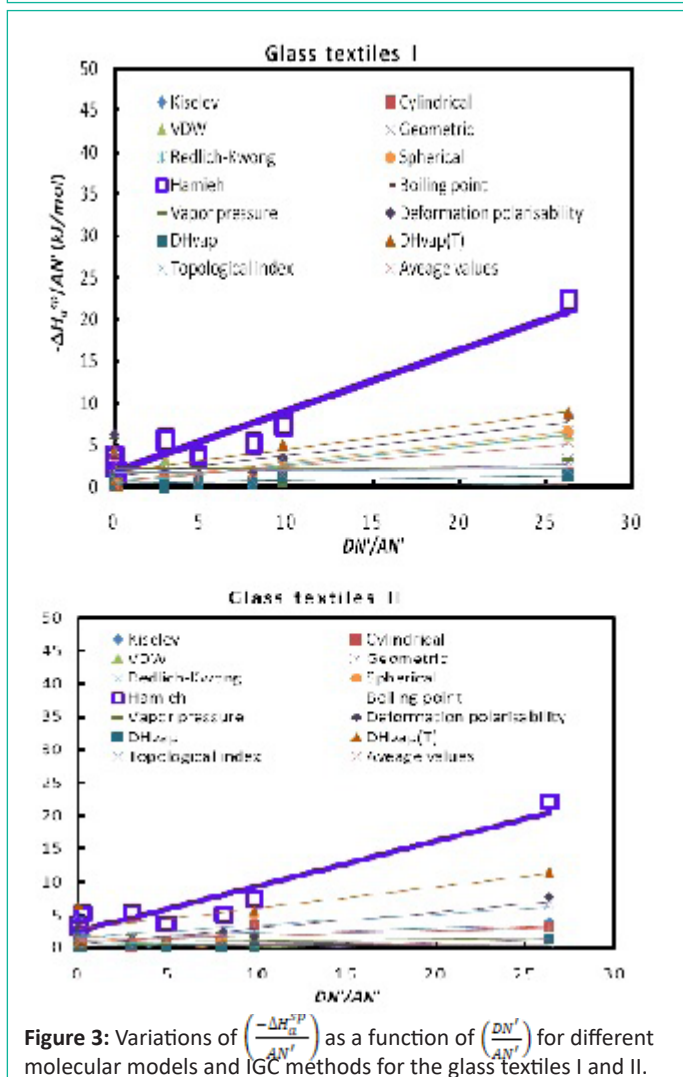


Figure 3: Variations of $\left(\frac{-\Delta H_a^{SP}}{AN^{SP}}\right)$ as a function of $\left(\frac{DN^{SP}}{AN^{SP}}\right)$ for different molecular models and IGC methods for the glass textiles I and II.

and ω_D of glass textiles (Tables SI3), by using the various IGC methods and models.

The various classical methods and models gave smaller linear regression coefficient R^2 sometimes reaching 0.0506 and therefore cannot be considered as confident values. The accurate results obtained by using the thermal model showed an important difference in the acid-base constants that can be presented in Table 5.

Table 5 proved that both glass textiles I and II exhibited an amphoteric surface with more accentuated basic character (about 3.8 times more basic for the glass textiles II and 2.5 for the glass textiles I). The acidic character is the same for the two glass fibers. Whereas, the basic Lewis constant is 1.5 times

more important for the non-pretreated glass textiles than the pretreated textiles. This difference is due to the presence of some impurities and water molecules in the industrial textiles that can contribute to increase the acid-base force and more particularly its basic character.

Conclusion

The surface thermodynamic properties of two glass textiles (raw and pretreated glass fibers) were completely determined by inverse gas chromatography at infinite dilution. The principal and fundamental parameter obtained from this precious IGC technique is the retention volume of the adsorption of n-alkanes and polar organic molecules on the textile materials. The London dispersive energy of these fiber surfaces were determined by using eight molecular models and five IGC classical and new methods. The specific parameters of the glass textiles were obtained from the different models and methods. The only valid model was that based on the thermal effect on the surface area of organic solvents.

The determination of the enthalpy and entropy of the different polar solvents adsorbed on the glass textiles led to determine the Lewis's acid-base constants K_A and K_D and entropic acid base parameters ω_A and ω_D of the glass textiles and proved a very important amphoteric character with a basic character for the two glass textiles about three times larger than their acidic character. An important effect of the pretreatment on the specific properties was highlighted. It was proved that the surface specific characters of the different thermodynamic parameters decreased when the glass textiles when pretreated.

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Conflict of Interest

Author declares that there is no conflict of interest.

References

1. Truong VD, Noh HW, Kim DJ. Effects of adding short fibers on impact resistance of glass textile reinforced cementitious composites under direct tension. *Constr Build Mater.* 2023; 379: 131220.
2. Peled A, Mobasher B, Bentur A. *Textile reinforced concrete*, Modern Con. Taylor & Francis Group, LLC. 2017.
3. Richter M, Zastra BW. On the nonlinear elastic properties of textile reinforced concrete under tensile loading including damage and cracking. *Mater Sci Eng A.* 2006; 422: 278-84.
4. Silva Fde A, Butler M, Mechtcherine V, Zhu D, Mobasher B. Strain rate effect on the tensile behaviour of textile-reinforced concrete under static and dynamic loading. *Mater Sci Eng A.* 2011; 528: 1727-34.
5. Flansbjerg M, Williams Portal NW, Vennetti D, Mueller U. Composite behaviour of textile reinforced reactive powder concrete sandwich façade elements. *Int J Concr Struct Mater.* 2018; 12: 1-17.
6. Truong VD, Kim DJ. A review paper on direct tensile behavior and test methods of textile reinforced cementitious composites. *Compos Struct.* 2021; 263: 1-15.
7. Truong VD, Kim MO, Kim DJ. Feasibility study on use of waste fishing nets as continuous reinforcements in cement-based matrix. *Constr Build Mater.* 2021; 269: 1-15.

8. Truong VD, Lee DH, Kim DJ. Effects of different grips and surface treatments of textile on measured direct tensile response of textile reinforced cementitious composites. *Compos Struct.* 2021; 278: 1-23.
9. De Munck M, El Kadi M, Tsangouri E, Vervloet J, Verbruggen S, Wastiels J et al. Influence of environmental loading on the tensile and cracking behaviour of textile reinforced cementitious composites. *Constr Build Mater.* 2018; 181: 325-34.
10. Bompadre F, Donnini J. Surface modification of glass textile for the reinforcement of a cement-based composite: a review. *Appl Sci.* 2021; 11: 1-19.
11. Karger-Kocsis J, Mahmood H, Pegoretti A. Recent advances in fiber/matrix interphase engineering for polymer composites. *Prog Mater Sci.* 2015; 73: 1-43.
12. Chen J, Zhao D, Jin X, Wang C, Wang D, Ge H. Modifying glass fibers with graphene oxide: towards high-performance polymer composites. *Compos Sci Technol.* 2014; 97: 41-5.
13. Luo N, Zhong H, Yang M, Yuan X, Fan Y. Modifying glass fiber surface with grafting acrylamide by UV-grafting copolymerization for preparation of glass fiber reinforced PVDF composite membrane. *J Environ Sci (China).* 2016; 39: 208-17.
14. Trzepieciński T, Batu T, Kibrete F, Lemu HG. Application of composite materials for energy generation devices. *J Compos Sci.* 2023; 7: 55.
15. Busch R, Philibert T. Le composite tissu de verre fin: la réponse industrielle à la miniaturisation de l'électronique. *Composites.* 1997; 7: 48-53.
16. Conder JR, Young CL. Physical measurements by gas chromatography Wiley J, editor and Sons. New York. 1979.
17. Sawyer DT, Brookman DJ. Thermodynamically based gas chromatographic retention index for organic molecules using salt-modified aluminas and porous silica beads. *Anal Chem.* 1968; 40: 1847-53.
18. Saint Flour C, Papirer E. 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.* 1982; 21: 337-41.
19. Saint Flour C, Papirer E. 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.* 1982; 21: 666-9.
20. Schultz J, Lavielle L, Martin C. The role of the interface in carbon fibre-epoxy composites. *J Adhes.* 1987; 23: 45-60.
21. Dorris GM, Gray DG. Adsorption of n-alkanes at zero surface coverage on cellulose paper and wood fibers. *J Colloid Interface Sci.* 1980; 77: 353-62.
22. Fowkes FM. In: Andrade JD, editor. Surface and interfacial aspects of biomedical polymers. Vol. I. New York: Plenum Press. 1985; 337-72.
23. Donnet JB, Park SJ, Balard H. Evaluation of specific interactions of solid surfaces by inverse gas chromatography. *Chromatographia.* 1991; 31: 434-40.
24. Brendlé E, Papirer E. A new topological index for molecular probes used in inverse gas chromatography for the surface nanorugosity evaluation, 2. Application for the evaluation of the solid surface specific interaction potential. *J Colloid Interface Sci.* 1997; 2224: 217.
25. Brendlé E, Papirer E. A new topological index for molecular probes used in inverse gas chromatography for the surface nanorugosity evaluation, 1. *J Colloid Interface Sci.* 1997; 194: 207-16.
26. Gutmann V. The donor-acceptor approach to molecular interactions. New York: Plenum Press; 1978.
27. Hamieh T, Rezzaki M, Schultz J. 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 Interface Sci.* 2001; 233: 339-42.
28. Hamieh T, Schultz J. New approach to characterise physico-chemical 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. *J Chromatogr A.* 2002; 969: 17-25.
29. Hamieh T, Schultz J. New approach to characterise physico-chemical properties of solid substrates by inverse gas chromatography at infinite dilution. II. Study of the transition temperatures of poly(methyl methacrylate) at various tacticities and of poly(methyl methacrylate) adsorbed on alumina and silica. *J Chromatogr A.* 2002; 969: 27-36.
30. Hamieh T, Fadlallah MB, Schultz J. 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. *J Chromatogr A.* 2002; 969: 37-47.
31. Hamieh T, Schultz J. Etude par chromatographie gazeuse inverse de l'influence de la température sur l'aire de molécules adsorbées. *J Chim Phys.* 1996; 93: 1292-331.
32. Hamieh T, Schultz J. Study of the adsorption of n-alkanes on polyethylene surface – State equations, molecule areas and covered surface fraction. *C R Acad Sci IIb.* 1996; 323: 281-9.
33. Hamieh T, Schultz J. A new method of calculation of polar molecule area adsorbed on MgO and ZnO by inverse gas chromatography. *C R Acad Sci IIb.* 1996; 322: 627-33.
34. Hamieh T. Study of the temperature effect on the surface area of model organic molecules, the dispersive surface energy and the surface properties of solids by inverse gas chromatography. *J Chromatogr A.* 2020; 1627: 461372.
35. Hamieh T, Ahmad AA, Roques-Carmes T, Toufaily J. New approach to determine the surface and interface thermodynamic properties of H- β -zeolite/rhodium catalysts by inverse gas chromatography at infinite dilution. *Sci Rep.* 2020; 10: 20894.
36. Hamieh T. New methodology to study the dispersive component of the surface energy and acid-base properties of silica particles by inverse gas chromatography at infinite dilution. *J Chromatogr Sci.* 2022; 60: 126-42.
37. Hamieh T. New physicochemical methodology for the determination of the surface thermodynamic properties of solid particles. *AppliedChem.* 2023; 3: 229-55.
38. Dorris GM, Gray DG. Adsorption of n-alkanes at zero surface coverage on cellulose paper and wood fibers. *J Colloid Interface Sci.* 1980; 77: 353-62.
39. Chehimi MM, Abel M-L, Perruchot C, Delamar M, Lascelles SF, Armes SP. The determination of the surface energy of conducting polymers by inverse gas chromatography at infinite dilution. *Synth Met.* 1999; 104: 51-9.
40. Chehimi MM, Pigois-Landureau E. Determination of acid-base properties of solid materials by inverse gas chromatography at infinite dilution. A novel empirical method based on the dispersive contribution to the heat of vaporization of probes. *J Mater Chem.* 1994; 4: 741-5.