Surface thermodynamic analysis of cleaned silicoaluminate glass fibres

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Inverse gas chromatography has been used to measure the surface adsorption of alkane probes on cleaned silicoaluminate glass fibres. The thermodynamic variables (enthalpy, ΔH_A°; entropy, ΔS_A°; free energy, ΔG_A°) and the dispersive component of the surface free energy (γ_S^D) have been evaluated by the measurement of specific retention volumes of the alkanes on the silicoaluminate glass fibres. The effectiveness of the acetone extraction procedure and the thermal treatment for the cleaning of the samples was also evaluated. The London (dispersive) component of the surface free energy has been used as a measurement of surface contamination by comparing the results for the washed samples and thermal treated samples.

1. Introduction

It is generally accepted nowadays that the final performance of a composite material depends, to a large extent, on the adhesion of the polymer matrix to the reinforcing fibre and, therefore, on the quality of the interface which is formed between both solids [1]. In the interface region both stress transmission and stress distribution will take place. Hence, it is of interest to know more about the formation and behaviour of the interface and interphase domains where the properties are hardly predictable from theoretical considerations only. Several authors have reported an interrelation between the surface energy [2], the surface chemical composition and the mechanical strength of the interface. The values of the surface energy and the surface chemical composition of both fibre and matrix are important for predicting the mechanical and physical strength of composites.

Different factors (voids, fibre surface contamination) may influence the adhesion between the fibre and the matrix in composites. This adhesion is substantially dependent upon the thermodynamic properties and chemical composition of the fibre surface.

An effective method for studying the surface properties of solids is inverse gas chromatography at infinite dilution (IGC), [3–5]. The aim of this work is to study the surface thermodynamics of the silicoaluminate glass fibres and their surface contamination by means of inverse gas chromatography.

2. Experimental procedure

2.1. Gas chromatography stationary phase

The materials used as adsorbents were silicoaluminate glass fibres (48 SiO_2, 52 Al_2O_3 wt.%) supplied by Ferro Enamel Española S.A. In order to remove the residual processing aids, fibres were cleaned by two methods: (i) acetone extraction followed by drying under vacuum (sample A); (ii) thermal treatment at 600 °C for three hours (sample B). Their specific surface areas (BET) determined by nitrogen adsorption were 0.26 $m^2 g^{-1}$ for both of them. The apparatus used for N_2 adsorption was of the dynamic type employing a flow of a mixture of nitrogen and helium gas [6]. Adsorption or desorption was determined from changes in gas composition measured with a thermal conductivity detector. The reproducibility was better than 90%.

2.2. Sorbates

The n-alkanes (n-hexane to n-decane) were obtained by Merck and the purity was better than 99% in all cases. All alkanes were used without further purification. The sorbates n-nonane and n-decane were not measured in sample A because of the long time of adsorption. A 1 µl Hamilton syringe was used to inject very small amounts of solute in the vapour form. All peaks were detected with the highest possible sensitivity range of the flame ionization detector (FID), i.e. close to zero surface coverage.

2.3. Apparatus

Gas chromatographic measurements were carried out with a commercial Perkin Elmer Sigma 2B chromatograph fitted with dual FID. The experimental temperatures were 35, 40, 45, 50, 55, 60 and 65 °C. Column temperature was maintained between ± 1 °C throughout the measurements.

The experimental data given in the present study were obtained with a 1.5 m long teflon column of 4.5 mm internal diameter packed with 7 g of fibres.

Helium carrier gas had a flow rate of about $40 \text{ cm}^3 \text{ min}^{-1}$. Net retention volumes were verified to be practically independent of flow rate so that equilibrium conditions could be assumed. However they were dependent on injected volumes as we will show below. Column conditioning was attained by heating to 100 °C during 16 h under helium flow.

2.4. Inverse gas chromatography at infinite dilution (zero coverage)

IGC consists of the injection of a small amount of probes (n-alkanes) of known properties into the column containing the solid. The measurement of the retention times of these probes at infinite dilution or near zero surface coverage, allows to determine the interactions between the probes and the solid in the absence of interactions between the probe molecules themselves.

The net retention volume V_N is calculated from

$$V_N = jD(t_R - t_0) \tag{1}$$

where t_R is the retention time of the given probe; t_0, the zero retention reference time measured with a non adsorbing probe such as methane; D the flow rate and j a compressibility factor of the gas.

The net retention volume is constant and independent of the vapour concentration in the gas phase when the Henry's law region is considered. Under our experimental conditions (absorbent with very low specific area) several amounts of probes were injected into the column and the retention volume at infinite dilution was extrapolated from the plot V_N versus sorbate pressure. Experimental V_N values were obtained at zero sorbate pressure.

It can be assumed that the adsorbate behaves as an ideal gas when the adsorption process takes place in the Henry's law region and the adsorbate concentration, in both the vapour and the adsorbent phases, are very low. In this region, lateral interactions are negligible and the thermodynamic functions only depend on adsorbate–adsorbent interactions.

Under these conditions, the differential heat of adsorption of the adsorbate, q_d, at zero coverage is equal to the standard differential enthalpy of adsorption, ΔH_A° and may be obtained from the Gibbs–Helmholtz equation

$$\ln V_N = -\frac{\Delta H_A^\circ}{RT} + C \tag{2}$$

assuming that ΔH_A° is independent of T in a narrow temperature range.

The partition coefficient K_S is related to the retention volume V_N by

$$K_S = \frac{V_N}{A} \tag{3}$$

where A is the total sample surface area. Substituting Equation 3 in Equation 2 we obtain the following expression

$$\ln(K_S A) = -\frac{\Delta H_A^\circ}{RT} + C \tag{4}$$

$$\frac{d(\ln K_S)}{d(1/T)} = \frac{q_d}{R} \tag{5}$$

Assuming that q_d is temperature independent, Equation 5 gives a linear relationship between $\ln K_S$ and $1/T$.

The variation in the standard free energy of adsorption is equal to the free energy of desorption and is given by

$$\Delta G_D^\circ \equiv \Delta G_A^\circ = -RT \ln\left(\frac{V_N P_0}{A \pi_0}\right) \tag{6}$$

where ΔG_A° is the free energy of desorption (or adsorption) of one mole of solute from a reference adsorption state defined by the bidimensional spreading pressure π_0 of the adsorbed film to a reference gas phase state defined by the partial pressure P_0 of the solute.

There are several approaches to choosing the standard surface state [7]. We used de Boer's, where $P_0 = 101 \text{ mNm}^{-2}$ (1 atm) and π is equal to 0.338 mNm^{-1}. The latter value defines the standard surface pressure as the pressure where the average distance of separation between molecules in the adsorbed phase equals that in the standard gas phase.

If both the standard differential enthalpy and the standard free energy of adsorption are known, the standard entropy of adsorption can be calculated by the equation

$$\Delta S_A^\circ = -\frac{(q_d + \Delta G_A^\circ)}{RT} \tag{7}$$

3. Results

First we have studied the cleaned silicoaluminate glass fibres by Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) spectroscopies in order to determine if the cleaning process produces any alteration on the structure of these fibres. Fig. 1 shows the infrared spectra of acetone washed fibres (sample A) and heated fibres at 600 °C (sample B). Both spectra present the broad band at 3400 cm^{-1} and the medium band at 1635 cm^{-1} which are associated with the stretching and bending vibrations of OH groups and molecular water [8]. The strong absorption bands at 1092, 805 and 441 cm^{-1} correspond to the different modes of Si–O–Si and O–Si–O vibrations [8]. Actually, these broad bands correspond to the sum of bands which appear overlapped in the same spectral region. These overlapped bands correspond to Al related bonds (Al–O–Si, AlO_4). We have assigned the medium and broad band at 654 cm^{-1} to the Al–O–Al stretching vibration.

X-ray diffraction (Fig. 2) shows that the studied fibres remain unchanged after the cleaned treatment. The XRD pattern presents the typical diffractogram of a glassy system. Therefore from infrared (i.r.) and XRD analysis the clean treatments do not alter the bulk structure of silicoaluminate glass fibres.

In order to study surface changes produced by cleaned treatments IGC was employed. Net retention volumes, V_N, were obtained from the maxima of the chromatographic peaks and the dead volume. The partitioning coefficient, K_S, is the relation between V_N and the surface area given by the amount of adsorbent in the column (Equation 3).
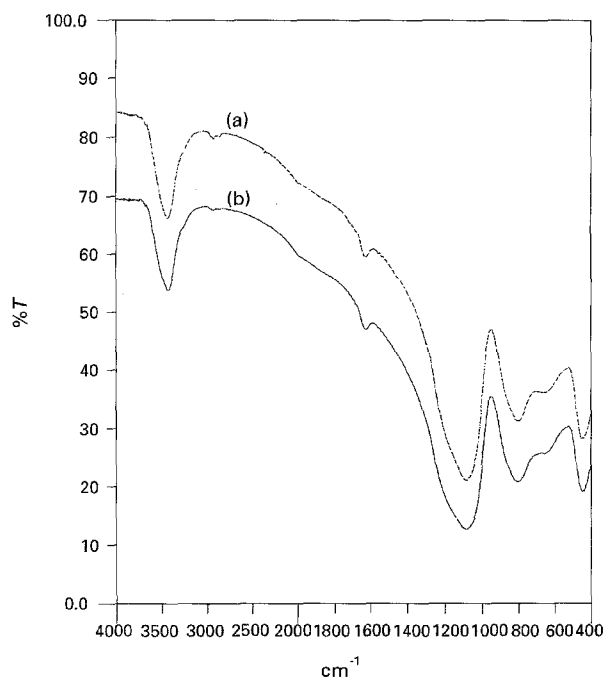
Figure 1 Fourier transform infrared spectra of (a) acetone washed and (b) heated silicoaluminate glass fibres.
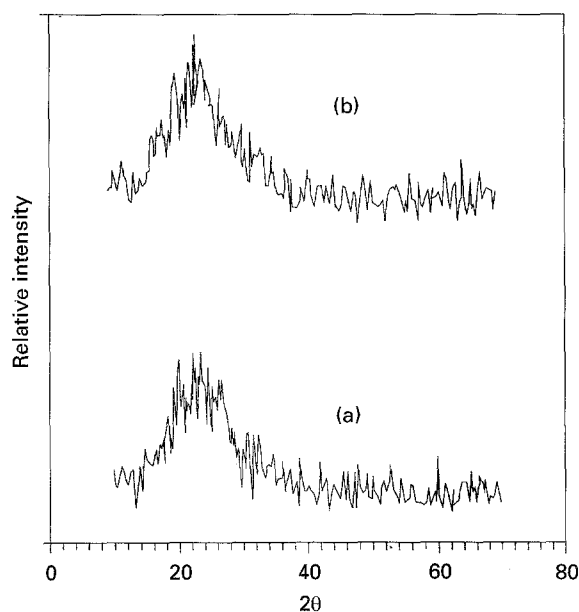

Figure 3 Retention volumes of n-octane on cleaned silicoaluminate glass fibres at 35 and 55 °C against the adsorbate pressure. □, heated fibres, 55 °C; ■, heated fibres, 35 °C; ◇, acetone washed fibres, 55 °C; ◆, acetone washed fibres, 35 °C.

Figure 2 X-Ray diffraction patterns of (a) acetone washed and (b) heated silicoaluminate glass fibres.

Figure 4 Variation of the Henry's law coefficients with reciprocal temperature for the adsorption of n-alkanes (C_6–C_8) on acetone washed silicoaluminate fibres. □, C_6; ◇, C_7; +, C_8.

The overall precision of V_N and K_S is dependent upon the errors in flow rate measurements, of the variations of flow rate and temperature during the experiment and of the measurement of the column dead volume, V_M. The accuracy of the K_S values are furthermore dependent upon the accuracy of the surface area.

To ensure that alkane adsorption was occurring under equilibrium conditions, different small volumes were injected in a Hamilton syringe and the retention volume was obtained by extrapolation as we have said above. Fig. 3 shows the retention volume of n-octane versus adsorbate pressure. These plots were fitted to a parabolic curve.

The variation of the Henry's law constants with temperature is illustrated in Fig. 4 and Fig. 5 for
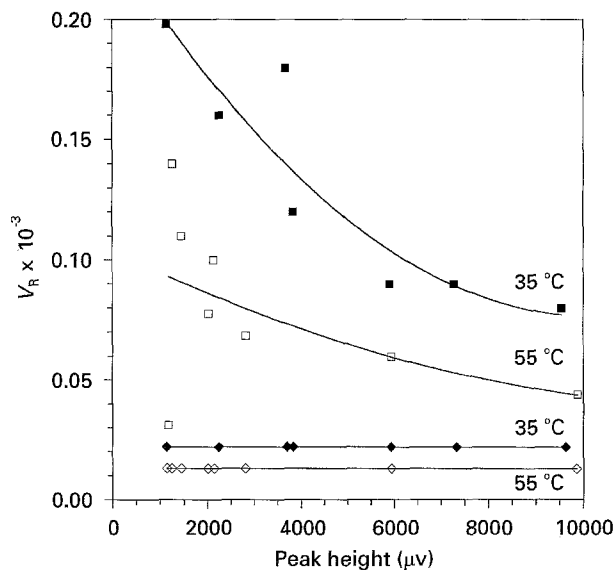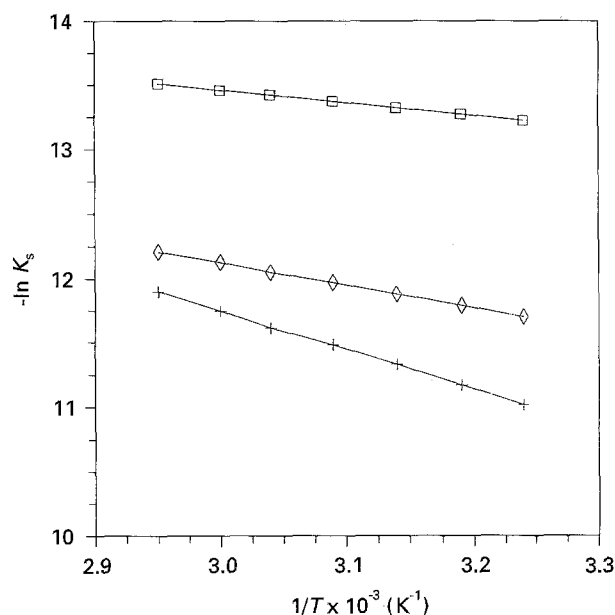
acetone washed fibres and heated fibres, respectively. These plots were found to be linear for all vapours on all samples, thereby confirming the validity of Equation 2. The adsorption of a given hydrocarbon decreases with increase in temperature, in accordance with a physical adsorption process. The q_d values were calculated from the slopes of the straight lines obtained, adjusted by least squares method. These values are given in Table I together with other thermodynamic variables (entropy ΔS_A°; free energy ΔG_A°; theoretical entropy $-({}_3S_t - {}_2S_t)$) obtained from Equations 6 and 7 at 50 °C. The ΔG_A° values were used to calculate the dispersive component of London.
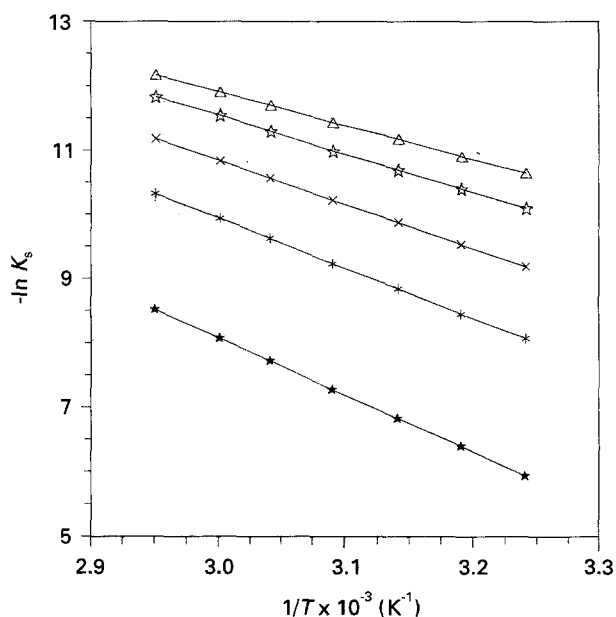
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Figure 5 Variation of the Henry's law coefficients with reciprocal temperature for the adsorption of n-alkanes (C_6–C_{10}) on heated silicoaluminate fibres. $\triangle$, C_6; $\star$, C_7; $\times$, C_8; $*$, C_9; $\bigstar$, C_{10}.

TABLE I Standard thermodynamic functions and theoretical entropy ($-(_3S_t - _2S_t)$) at 50 °C for the zero coverage adsorption of n-alkanes on silicoaluminate glass fibres. (A) Acetone washed fibres. (B) Heated fibres)

Samples		q_d (kJ mol^{-1})	ΔG_A° (kJ mol^{-1})	ΔS_A° (J K^{-1} mol^{-1})	$(-(_3S_t - _2S_t))$ (J K^{-1} mol^{-1})
C_6	A	6.55	16.36	−30.35	52.05
	B	39.53	21.44	55.98	
C_7	A	12.8	20.11	−22.62	52.68
	B	45.62	22.61	71.2	
C_8	A	23.32	21.42	−5.88	53.22
	B	52.88	24.68	87.26	
C_9	B	60.5	27.33	102.64	53.70
C_{10}	B	69.64	32.58	114.68	54.14

4. Discussion

Sample B (Fig. 5) shows higher values of K_S than sample A (Fig. 4) in accordance with a highest interaction with the sorbate probes. For both samples the K_S values increase with the number of carbon atoms from the n-hexane to n-octane. Sample A shows low differential heats of adsorption indicating a low concentration of high energy sites on silicoaluminate glass fibres. There is a great difference in the interaction energy between the two samples. Sample B has a higher interaction with the adsorbate than sample A; nevertheless, the low isosteric heat values for both samples are in accordance with a low concentration of high energy sites indicating non-specific adsorption. The difference between q_d values for both samples decreased from n-hexane to n-octane.

The values of the thermodynamic data (given in Table I) vary linearly with the number of carbon atoms. The increment per $-CH_2-$ in the enthalpy of adsorption is not a constant value, which is not in accordance with a flat orientation of the isolated n-alkane molecule on the surface of silicoaluminate glass

fibres [4]. There is a great difference in the thermodynamic data of the two samples.

The free energies ΔG_A° increase with the carbon atom number correspondingly to a more spontaneous process. ΔG_A° values are higher on heated samples than washed samples. This can be explained by the higher surface hydroxyl group content of the B sample, which in turn results in higher surface free energies. These results are in accordance with the isosteric heats.

The magnitude of ΔS_A° is related to the number of degrees of freedom lost upon adsorption, and to the mixing with surface contaminants [9]. The former represents a negative contribution of ΔS_A° and decreases its magnitude. The entropies of adsorption of alkanes on sample A are higher than the corresponding entropies found for adsorption on sample B. Besides, sample A shows positive entropy values which indicates the mobility of the adsorbate on the surface. For both samples this mobility decreased with the increase in the alkane length.

Entropies vary linearly with the number of carbon atoms (as shown in Table I). These experimental values were compared with those calculated from a theroretical model assuming the loss of one transitional degree of freedom of the adsorbate upon adsorption.

The three dimensional translation entropy, $_3S_t$, of the adsorbate as an ideal gas is given by

$$_3S_t = R\ln(M^{3/2}T^{5/2}) - 9.62 \qquad (8)$$

where M is the molar mass.

Similarly, the entropy of the adsorbate as an ideal, mobile, two dimensional gas may be calculated from

$$_2S_t = R\ln(MTA_S) + 275.32 \qquad (9)$$

where A_S is the area available for a molecule in the standard state and for an ideal gas ($A_S = 4.085 \times 10^{-16} \text{m}^2$ [10]).

The $_3S_t$ and $_2S_t$ values were obtained from Equations 8 and 9. The entropy change associated with the loss of one degree of freedom upon adsorption is given by $\Delta S_t = _3S_t - _2S_t$. The experimental and theoretical values of $T\Delta S$ are compared in Fig. 6. In sample B (heated sample) the ΔS_A° values obtained experimentally are higher than the ($_3S_t - _2S_t$) values when the length of the alkane probe increases. The important entropy decrease observed upon adsorption cannot be attributed to the loss of one degree of freedom of the adsorbed molecules. This additional entropy loss may result from a restriction of rotational and vibrational freedom on the surface. The same conclusion was found by other authors [4, 11]. On the other hand, for sample A (washed sample), the ΔS_A° values obtained experimentally are lower than the theoretical ones. In this case, we attribute the positive contribution to the entropy to the mixing between the adsorbed molecules and the surface contaminants. This mixing is the result of the mobility of the sorbate probes [9].

The low isosteric heats and the adsorption entropies indicate no specific interactions between n-alkanes and surface fibres. The non-specific interaction can be verified by Fig. 7. In this plot, we have represented
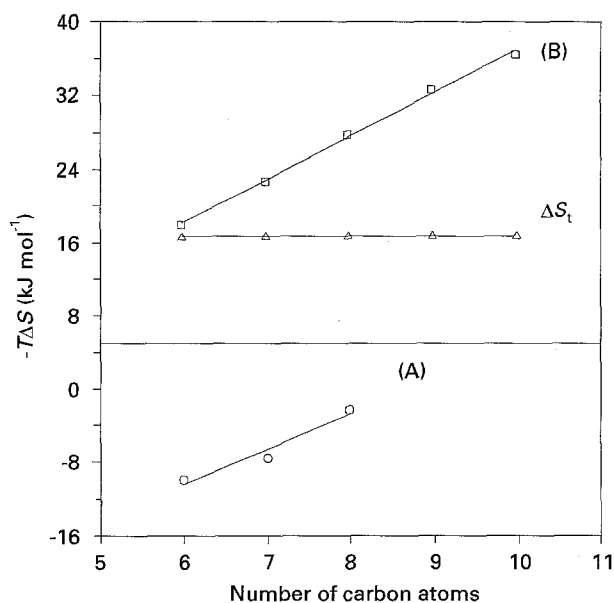
Figure 6 Adsoption entropy ($T\Delta S_A^\circ$) of n-alkanes versus number of carbon atoms of the adsorbates: (A) acetone washed sample, (B) heated sample ($\square$), (ΔS_t) the theoretical entropy changes ($\triangle$).
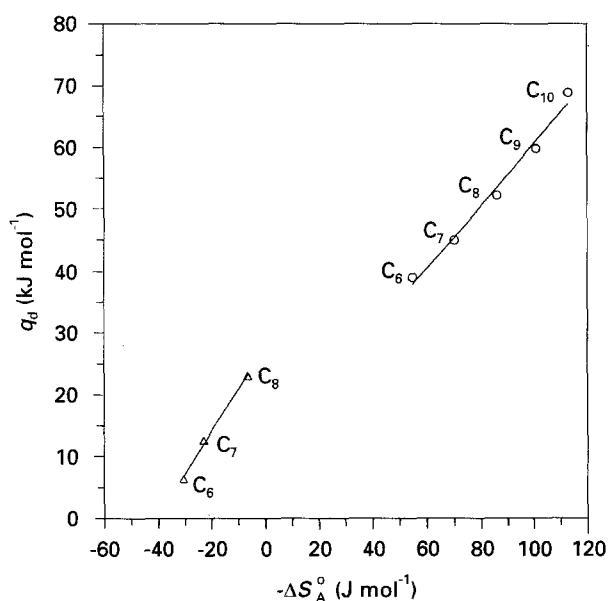

Figure 7 Variation of differential heats of adsorption (q_d) with the standard entropy of adsorption (ΔS_A°). $\bigcirc$, heated samples, 600 °C; $\triangle$, acetone washed samples.

the values of q_d as a function of ΔS_A° observing a linear relationship between them [12, 13]. In both samples, all experimental data lie on a straight line, indicating the effect commonly referred to in the literature as the compensation effect [13], which is due to no specific interactions.

When the adsorbates are saturated n-alkanes and do not possess permanent dipoles, the adsorption potential on a nonpolar surface is made up of a repulsive term and an attractive term due to London dispersive forces. Therefore for the two adsorbents studied here, the interaction with n-alkanes will occur predominantly through London dispersive forces. According to Fowkes [14] the energy of adhesion W_A, in the case of dispersive interactions is given by:

$$W_A = 2(\gamma_S^D \gamma_L^D)^{1/2} \qquad (10)$$

Dorris and Gray [4] use a method for the determination of γ_S^D by considering the increment of ΔG_A° per methylene group in the n-alkane series of general formula C_nH_{2n+2}. The increment $\Delta G_{(CH_2)}^\circ$ defined by

$$\Delta G_{C_{n+1}H_{2n+4}}^\circ - \Delta G_{C_nH_{2n+2}}^\circ$$

leads to

$$\gamma_S^D = \frac{\left(RT \ln \dfrac{V_N \cdot C_{n+1} \cdot H_{2n+4}}{V_N \cdot C_n \cdot H_{2n+2}}\right)^2}{4N^2 \cdot a_{CH_2}^2 \gamma_{CH_2}} \qquad (11)$$

where a_{CH_2} is the surface area of a CH_2 group (6 Å) and γ_{CH_2} the surface energy of a CH_2 group given by

$$\gamma_{CH_2} = 35.6 + 0.058(20 - T) \qquad (12)$$

The London component of the surface free energy, γ_S^D, was calculated from Equation 11 and was 34.72 mJ m^{-2} for acetone washed fibres and 39.35 mJ m^{-2} for heated fibres. These values are similar to those found by other authors in amorphous samples [15].

Chappell and Williams [9] showed the usefulness of the London component as a measurement of the surface contamination. They studied the effectiveness of a range of solvent extraction procedures. They observed how the London dispersive component increased from 32 mJ m^{-2} for the unwashed poly (p-phenyleneterephthalamide) (PPTA) fibres up to 65 mJ m^{-2} when they were washed thoroughly with an effective procedure. Tsutsumi and Ohsuga [15] evaluated the effect on the London dispersive component of the treatment of glass fibres with silane coupling agents. They found a value of 40 mJ m^{-2} for E-glass fibres and observed reductions of 20–50% depending on the type of silane coupling agent used. In this work, we have found 12% reduction in γ_S^D from 39.35 mJ m^{-2} for heated fibres to 34.72 mJ m^{-2} for acetone washed fibres. This reduction in the dispersive component of the free surface energy is attributed to the presence of processing aims on the surface fibres which are not removed with the acetone treatment. These results are in accordance with the higher isosteric heat values found for the heated sample compared to for ones of washed sample.

5. Conclusions

Inverse gas chromatography has been used as a surface study method and to monitor the surface contamination of silicoaluminate glass fibres. From the infinite dilution retention volumes, as a function of temperature, we have calculated the thermodynamic data ΔH_A°, ΔG_A°, ΔS_A° and the London dispersive component of acetone washed and heated samples. The results show the acetone washing is not effective in removing the processing aims. The heating at 600 °C yields to cleaned fibres. The surface contamination produces low energy surfaces with a London dispersive component of 34.72 mJm^{-2}. This value increases to 39.35 mJm^{-2} when the fibres are heated which indicates that the surface is cleaned completely. Values of ΔH_A° and ΔG_A° for heated samples are higher than

those for washed samples. Therefore the heat treatment produces more energetic surface, where sorbate probes are more localized in accordance with ΔS_A° values.

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