Use of inverse gas chromatography to characterize cotton fabrics and their interactions with fragrance molecules at controlled relative humidity

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Abstract

The present work focused on the surface characterization and fragrance interactions of a common cotton towel at different relative humidities (RHs) using inverse gas chromatography (IGC) and dynamic vapour sorption. The sigmoidal water sorption isotherms showed a maximum of 16% (w/w) water uptake with limited swelling at 100% RH. This means that water interacts strongly with cotton and might change its initial physico-chemical properties. The same cotton towel was then packed in a glass column and characterized by IGC at different relative humidities, calculating the dispersive and specific surface energy components. The dispersive component of the surface energy decreases slightly as a function of relative humidity (42 mJ/m^2 at 0% RH to 36 mJ/m^2 at 80% RH) which would be expected from swelling of the humidified cotton. The Gutmann's donor constant K_d increased from 0.28 kJ/mol at 0% RH to 0.42 kJ/mol at 80% RH, indicating that a greater hydrophilic surface exists at 80% RH, which is also as expected. Water, undecane and four fragrance molecules (dimetol, benzyl acetate, decanal and phenylethanol) were used to investigate cotton–fragrance interactions between 0 and 80% RH. The adsorption enthalpies and the Henry's constants were calculated and are discussed. The higher values for the adsorption enthalpies of polar molecules such as dimetol and phenylethanol suggest the presence of hydrogen bonds as the main adsorption mechanism. The Henry's constant of dimetol was also determined by headspace gas chromatography measurements at 20% RH, giving a similar value (230 nmol/Pa g by IGC and 130 nmol/Pa g by headspace GC), supporting the usefulness of IGC for such determinations. This work confirms the usefulness of chromatographic methods to investigate biopolymers such as textiles, starches and hairs.
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Keywords: Fragrances; Relative humidity; Thermodynamic parameters; Adsorption isotherms; Inverse gas chromatography; Cellulose

1. Introduction

The control of the relative humidity (RH) in inverse gas chromatography (IGC) allows us to

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detect, under real conditions, surface modifications on biopolymers such as cotton, starches and hairs. Cotton is widely used in the textile industry, representing more than 50% of the world textile fibre production [1]. For this reason, most companies test and evaluate fragrances on cotton [2]. Natural cotton, also called cellulose I, is composed of a mixture of microcrystalline and amorphous cellulose [1]. This ratio, in commercial cotton, depends on the process-

ing of the raw material and can reach about 0.5 (50% microcrystalline cellulose and 50% amorphous cellulose) after classical NaOH treatment (cellulose II). The surface and physico-chemical properties of the cotton fibres are consequently different to the original properties [1]. Study of fragrance interactions on cotton can help us to understand the adsorption mechanisms under ambient conditions or during drying/wetting steps. Several workers have already studied cotton and microcrystalline cellulose from a thermodynamic point of view using techniques such as microscopy, spectroscopy and contact angle [3–5]. To our knowledge, IGC has only been used for cellulose and cotton by Belgacem et al. [6], Dorris and Gray [7,8], Thielmann and Reutenauer [9], Balard et al. [10] and Gauthier et al. [11]. The IGC results obtained for cotton are not trivial to interpret due to the complexity of the cellulose or cotton surface. Furthermore, the infinite dilution method relates to the highest energy sites of the polymer assuming a planar surface and this does not represent the real cotton surface [10]. Nevertheless, this technique allows one to detect modifications in the surface properties of different cotton samples induced by industrial treatments or changes induced by factors such as thermal expansion or swelling in the presence of water. Balard et al. [10] determined the dispersive and specific components of the surface energy at different temperatures and 0% relative humidity (39.0 mJ/m^2 at 40 °C and 34.5 mJ/m^2 at 60 °C). They completed their work characterizing the specific interactions by injections of a series of halogenoalkanes, alcohols and aromatic compounds. They were thus able to determine the specific interaction of a functional group on the cotton surface such as an hydroxyl group (-12.4 kJ/mol). They also determined the acid–base constants of the cotton using Gutmann's method [$K_a = 654$ (dimensionless) and $K_d = 984$ J/mol], but these values were not confirmed by other authors [12]. Nevertheless, that work is the most complete cotton surface study performed using IGC, highlighting the potential and the limitations of the method.

The present work was also focused on the characterization and comparison with literature values of a common cotton towel surface, but the main effort was directed towards the determination of the interaction forces between a common, uncoloured cotton towel and selected fragrance molecules. This was done using an IGC instrument, allowing us to monitor accurately the temperature and the relative humidity of the system. In the case of cotton, the microcrystalline part can be associated with gas–solid interactions (adsorption), while the amorphous part is associated with the absorption mechanism, in particular when water is injected. Publications on microcrystalline celluloses and their adsorption properties can be found elsewhere, especially in the pharmaceutical literature. The role of amorphous cellulose in the absorption mechanism was well described by Morton and Hearle [1].

2. Experimental

The cotton towel was supplied by the Firmenich Perfumery Division and corresponds to a common uncoloured and unflavoured reference cotton. No surface treatment was applied before or during the experiments.

The experiments were divided into three parts: the first part was dedicated to the determination of the water sorption isotherms of a common cotton towel at 20 °C. The second part was dedicated to the surface characterization of the cotton towel in terms of dispersive and specific components of the surface energy by IGC. Finally, the cotton–fragrance molecule interactions were also investigated by IGC.

2.1. Water sorption isotherm

The water sorption isotherm was obtained using a dynamic vapour sorption (DVS) device from Surface Measurement System (London, UK). Small pieces of the original cotton towel were placed in a small DVS pan and the temperature set at 20 °C. The relative humidity program was started at 0% RH and terminated at 100% RH with a 10% RH step increase when thermodynamic equilibrium was reached (mass change <0.005 mg/min). The duration of the sorption isotherm experiment was about 24 h.

2.2. Inverse gas chromatography

The inverse gas chromatograph was a HP6890 from Hewlett-Packard (Palo Alto, CA, USA), modi-

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fied by Surface Measurement System. An external oven was used in the configuration because of the need for high temperature control (200 °C versus 90 °C for the standard configuration). The humidity control could be set from 0 to 95% RH. Automatic pulsed injections were available as well as manual injections at infinite dilution. Finite concentration could also be performed, but this injection method was not used during this work. The glass column was 1.8 m×3 mm I.D. Packing was performed by cutting small pieces of the cotton towel and using a vacuum pump to compact the fibres as much as possible. The cotton was then placed in the IGC oven and dried overnight at 0% RH and 130 °C. The mass of dried cotton in the column was 1.16 g. Two other, shorter columns (60 cm) containing 0.32 and 0.25 g of the same cotton towel were used to confirm the results obtained with the first column.

The retention time determined at peak maximum for a symmetrical peak allows the calculation of the net retention volume V_n (Eq. (1)) and the specific retention volume V_g^0 (Eq. (2)). From these data, several thermodynamic properties can be calculated as described [13,14]:

$$V_n = jF(t_r - t_m) \tag{1}$$

$$V_g^0 = \frac{jF(t_r - t_m)}{w} \cdot \frac{273.15}{T_c} \tag{2}$$

where j is the James and Martin pressure drop correction:

$$1.5 \cdot \left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right] \tag{3}$$

F is the carrier gas flow-rate (ml/min), t_r is the retention time at peak maximum (min), t_m is the retention time of a non-interacting probe (min), w is the mass of the stationary phase (g), T_c is the temperature of the column (K), p_i is the pressure at the inlet (Pa), and p_o is the pressure at the outlet (Pa).

2.3. Characterization of the cotton surface

The surface can be characterized using the dispersive and acid–base components of the surface energy as defined by Fowkes [15] (dispersive forces) and Gutmann [16] (acid–base components). These approaches were used here despite the on-going discussion about the correct interpretation of the specific components of the surface energy [17]. A series of *n*-alkanes (hexane, heptane, nonane and decane from Merck, Darmstadt, Germany) was injected at infinite dilution to determine the dispersive component of the surface energy. Acetone, tetrahydrofuran, chloroform and ethyl acetate (Merck) were injected at infinite dilution to determine the specific components of the surface energy. Infinite dilution is obtained when the peak is symmetric and the retention time reproducible. In general, the injection of a few microliters (1 to 10) of the solvent vapour phase is sufficient to reach infinite dilution conditions. The temperature range was from 40 to 80 °C, while the relative humidity varied from 0 to 80% RH. Furthermore, the specific surface area by the BET method and the true density were determined using a NOVA 1200 instrument (Quantachrome, Munich, Germany) to complete the overall physico-chemical characterization of the cotton towel.

Fowkes' equation for the determination of the dispersive component of the surface energy is:

$$RT \ln V_N = 2N_A(\gamma_s^d)^{1/2} \cdot a(\gamma_L^d)^{1/2} \tag{4}$$

where R is the gas constant, T the temperature of the column, N_A Avogadro's number ($6.023 \cdot 10^{23}$), a the surface of the methylene group ($-CH_2-$) (m^2/mol), γ_s^d the dispersive component of the surface energy of the solid (J/m^2), and γ_L^d the dispersive component of the adsorbed fluid (J/m^2).

Gutmann's equation for the calculation of the acid–base components of the surface energy is:

$$\Delta H_{sp}/AN_1 = DN_2 + AN_2 \cdot DN_1/AN_1 \tag{5}$$

where ΔH_{sp} is the specific enthalpy of adsorption (kJ/mol), AN_1 the acceptor constant of the injected probe, $AN_2 = K_a$ the acceptor constant of the stationary phase, DN_1 the acceptor constant of the injected probe (kJ/mol) and $DN_2 = K_d$ the donor constant of the stationary phase (kJ/mol).

2.4. Characterization of fragrance interactions on cotton

Water (deionized), undecane (Merck) and four

fragrance molecules (dimetol, decanal, phenylethanol and benzyl acetate from Firmenich Perfumery Division) were injected at infinite dilution to determine the enthalpy (Eq. (6)) and entropy of adsorption (Eq. (7)) as well as the Henry's constant per gram of adsorbent (Eq. (8)). The temperature range was from 40 to 80 °C and the relative humidity varied from 0 to 80% RH. For water, the relative humidity remained constant at 0% and the temperature range varied from 100 to 190 °C. The equations allowing the calculation of the enthalpy of adsorption, entropy of adsorption and Henry's constant, assuming temperature independence, are the following:

$$\Delta H_a = - R \cdot d[\ln(V_N/T)]/d(1/T) \tag{6}$$

$$\Delta S_a = (\Delta H_a - \Delta G_a)/T \tag{7}$$

$$He = V_N/(mRT) \tag{8}$$

where ΔH_a is the enthalpy of adsorption (kJ/mol), ΔG_a is the free energy of adsorption (kJ/mol), ΔS_a is the entropy of adsorption (J/mol K), He is Henry's constant (mol/Pa g), m is the mass of the stationary phase (g) and T is the temperature of the stationary phase (K).

3. Results and discussion

3.1. Water sorption isotherms

The shape of the water sorption isotherm is sigmoidal, which confirms the experiments described in previous reports on cellulose [10,11]. The maximum water uptake at 100% RH is about 16% (w/w) at 20 °C with limited swelling. Synthetic textiles such as polyesters take up less than 1% (w/w) of water under the same conditions of temperature and relative humidity. The two cellulose structures play a different role in taking up water: by adsorption (surface) or absorption (bulk) mechanisms. Microcrystalline cellulose is responsible for the adsorption mechanisms, while amorphous structures are responsible for the high water uptake by absorption mechanisms [1]. Balard et al. [10] used an IR method to determine the crystalline/amorphous cel-
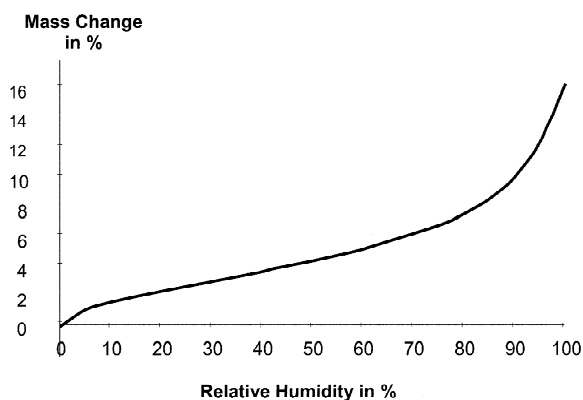

Fig. 1. Water sorption isotherm at 30 °C determined by dynamic vapour sorption. The sigmoidal shape and the limited swelling at high relative humidities are characteristic of biopolymers such as cellulose.

lulose ratio, but this method needs to be confirmed by other authors before it can be used as a reference.

Fig. 1 shows the sigmoidal water sorption isotherms of an uncoloured cotton towel at 20 °C. The amount of sorbed water reached about 16% (w/w) at 100% RH, which is in the lower range of literature values (15–25%).

3.2. Characterization of the cotton surface

The dispersive component of the surface energy gives an estimate of the heterogeneity of the surface [6,18–20]. Any change of the cotton structure might influence the dispersive surface energy. An increase in temperature without any structure change might slightly decrease the γ_s^d value due to expansion of the cotton. An increase in the relative humidity from 0 to 20, 50 and 80% RH changes the structure of the cotton by swelling and might decrease the γ_s^d value slightly, which is also the case summarized in Table 1.

Table 1
Influence of temperature and relative humidity (RH) on the γ_s^d value of a cotton towel

Temp. (°C)	γ_s^d (mJ/m^2)			
	0% RH	20% RH	50% RH	80% RH
40	42±1	42±1	40±1	36±2
45	40±1	41±1	39±1	36±1
50	42±2	41±1	38±1	35±1

These values confirm previous work on cellulose [10]. The slight, but significant, decrease of γ_s^d as a function of temperature is due to thermal expansion of the cellulosic sample. The slight decrease of γ_s^d as a function of relative humidity is due to swelling of the cotton in the presence of water. The γ_s^d value of water is 21.8 mJ/m^2 at 20 °C [21] and if a simple additive law is considered in the case of mixing, it is then obvious that γ_s^d of wetted cellulose decreases as a function of relative humidity. Furthermore, if the amorphous phase is mainly responsible for water uptake, these results show that a change of the amorphous structure (penetration of water molecules into the amorphous phase or opening of hydrophilic sites by water molecules) does not affect the heterogeneity of the cotton surface, or only to a relatively small extent.

A more interesting investigation is the Lewis acid–base or electron donor–acceptor character of the cotton surface and its change as a function of relative humidity. Gutmann's approach was chosen to calculate the acidic and basic constants of the cotton surface. Fig. 2 and Table 2 summarize the results.

Table 2
Gutmann's acid–base constants for the cotton towel at different relative humidities

	Relative humidity			
	0%	20%	50%	80%
K_d (kJ/mol)	0.28	0.30	0.36	0.42
K_a	0.03	0.01	0.04	0.05

The values of the constants K_a and K_d at 0% RH confirm previous work on cellulose [12]. Table 2 shows that the surface of cotton is obviously hydrophilic. An increase in the relative humidity of the system suggests the activation of more hydrophilic sites by the water molecules and logically the surface becomes more hydrophilic. The specific surface area measured using the BET method was estimated to be 1.0 ± 0.5 m^2/g, which is in good agreement with literature data [1].

3.3. Characterization of fragrance interactions with the cotton towel

The strength of an interaction between the cotton towel and a molecule can be correlated with its
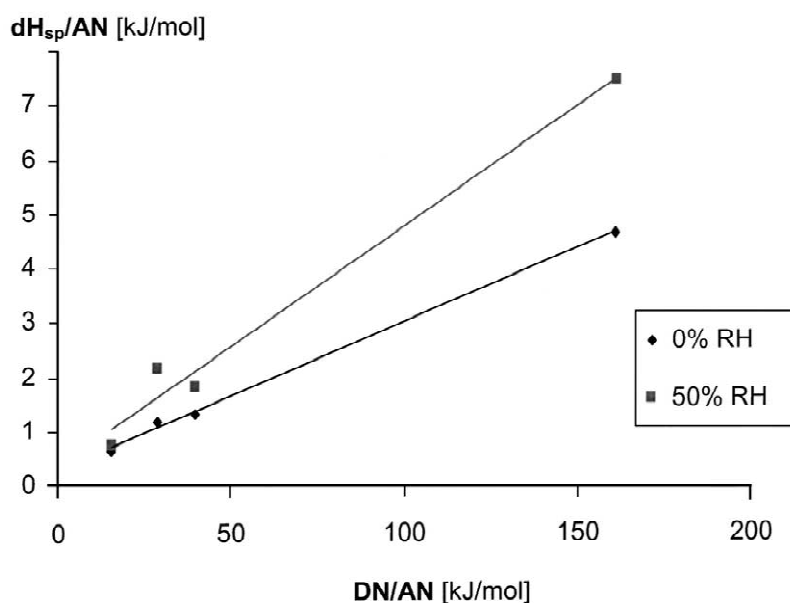

Fig. 2. Acid–base surface characterization of a cotton towel at 40 °C and 0–50% RH. Application of Gutmann's theory at two different relative humidities (0 and 50% RH). Linear regressions were performed to calculate the acceptor and donor constants (K_a and K_d) of the cotton towel.
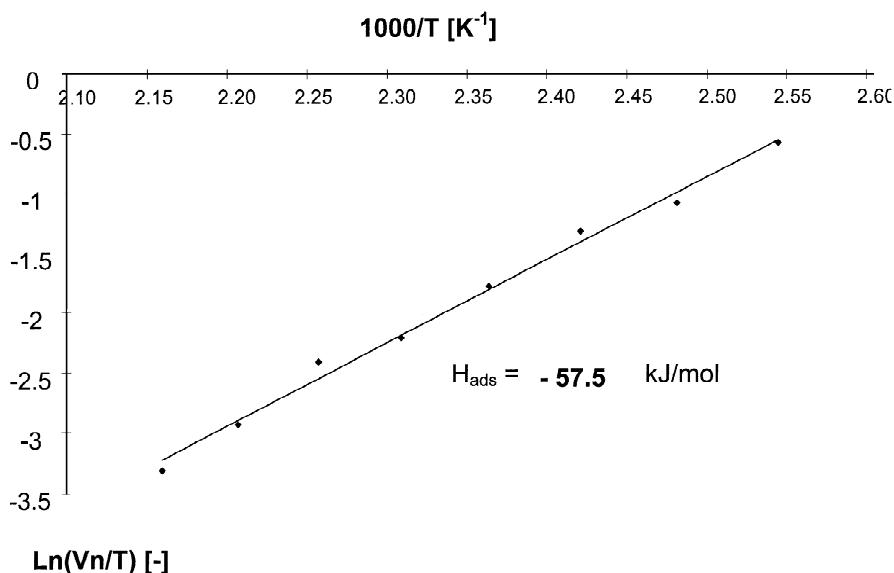
1000/T [K⁻¹]

Fig. 3. Water–cotton towel interactions determined by infinite dilution injections of water vapour at 0% RH. The enthalpy of adsorption ($\mathrm{d}H = -57.5$ kJ/mol) suggests the presence of H-bonding between the cotton surface and the water molecules.

enthalpy of adsorption. Assuming that this enthalpy remains constant in the experimental range of temperatures, the graphs shown in Fig. 3 were plotted and the enthalpy of adsorption calculated from the slopes.

The exact retention mechanism of water on cotton is still under investigation owing to its complexity, but it was assumed in this work that the amorphous phase tends to absorb, while the microcrystalline structure tends to adsorb, molecules. In the case of water, absorption seems to be the main retention mechanism. This explains the need to heat to high temperature (>100 °C) to desorb the injected water molecules. The value -57.5 kJ/mol represents the enthalpy of absorption, which cannot be compared with any adsorption enthalpies calculated below. This value can be compared with the enthalpy of vaporization of water (-40.7 kJ/mol [22]). The difference between the enthalpy of vaporization of water at 100 °C and the enthalpy of absorption of water on cotton is -16.8 kJ/mol, which suggests the presence of specific interactions (H-bonding) able to retain water molecules strongly above 100 °C [23].

Fig. 4 shows the influence of the highly polar hydroxyl group in phenylethanol and dimetol compared with an aldehyde group (decanal) or an ester

group (benzyl acetate). This experiment was performed at 0% RH and suggests that the hydroxyl groups are oriented in such a way so as to induce stronger interactions with the highly hydrophilic cotton surface (H-bonding).

Fig. 5 shows the difference between an alkane (undecane) and a polar molecule (dimetol) at 20% RH. The presence of water causes a large difference in the system in terms of the strength of the interaction. Adsorption on a surface containing adsorbed and absorbed water cannot, however, be directly compared with adsorption at 0% RH (binary system). Table 3 shows the enthalpy of adsorption, the entropy of adsorption and Henry's constant of undecane and dimetol at different relative humidities.

These data are very interesting as they show the direct effect of relative humidity on the volatility of the molecules (Henry's constant) as well as the random or non-random adsorption mechanisms reflected by ΔS. The adsorption of undecane is random at 0% RH, while, at 20% RH, the adsorption process is not random, indicating that undecane molecules have to find more adapted adsorption sites. Furthermore, the increase in the enthalpy of adsorption of undecane when the RH increases from 0 to 20% is still under investigation. The presence of a ternary
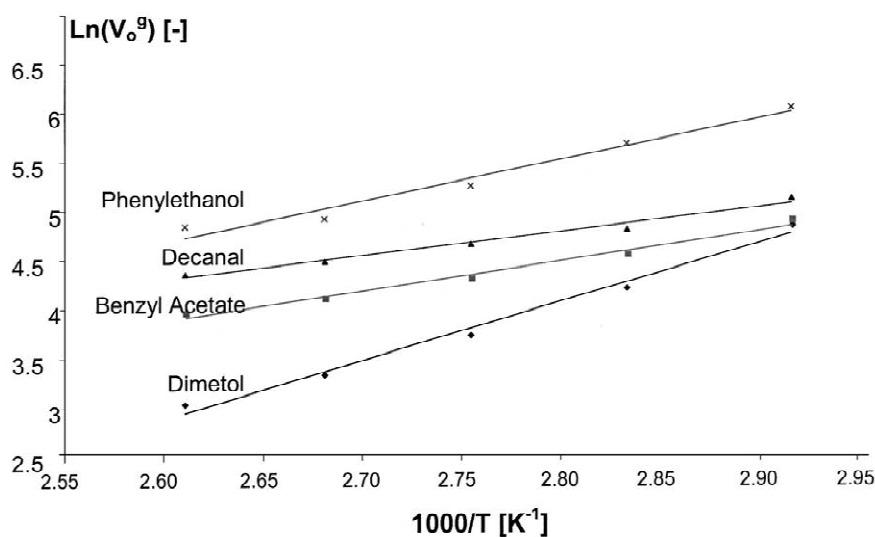
Fig. 4. Four fragrance molecule–cotton towel interactions at 0% RH. The difference in slopes suggests different strengths of interactions. The hydroxyl groups of phenylethanol and dimetol contribute to stronger interactions.

system at RH >0% also induced interactions between water sorbed in cotton and undecane, which increases the total enthalpy of adsorption. Dimetol, on the other hand, shows a non-random interaction, even at 0% RH, indicating the presence of oriented interactions between the molecules and the cotton surface (H-bonding). Headspace gas chromatography

(HS-GC) was performed by an internal laboratory on the same cotton towel at 25 °C and 20% RH. Dimetol was deposited and the closed system was stabilized for 72 h before quantifying the dimetol in the headspace by GC–flame ionization detection. Henry's constant per gram of adsorbent determined by HS-GC was 130 nmol/Pa, while 230 nmol/Pa
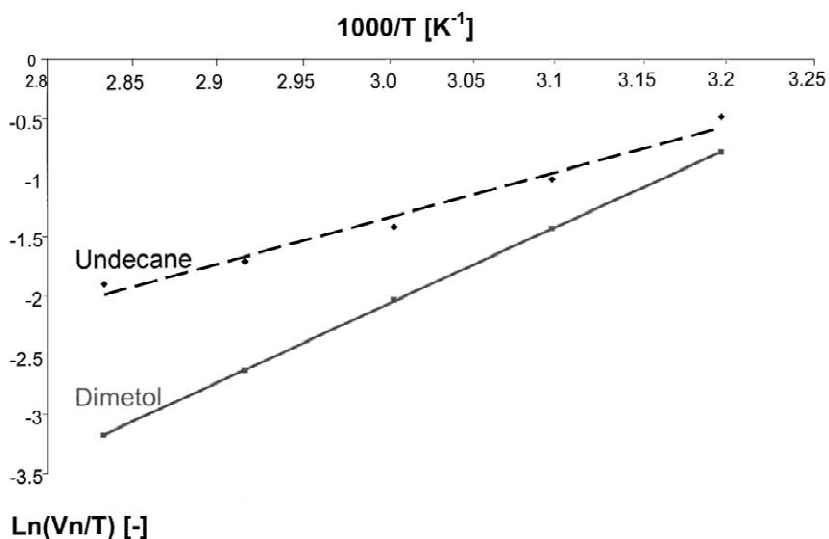

Fig. 5. Dimetol/undecane–cotton interaction at 20% RH.

Table 3
Henry's constant, enthalpy of adsorption (dH) and entropy of adsorption (dS) of undecane and dimetol

Relative humidity	Henry's constant (nmol/Pa g)	dH (kJ/mol)	dS (J/mol K)
Undecane			
0%	54	−33	−11
20%	40	−54	−84
50%	34	−56	−92
80%	26	−56	−91
Dimetol			
0%	350	−70	−112
20%	210	−71	−119
50%	160	−81	−148
80%	96	−78	−147

was calculated by IGC. The order of magnitude is good and an explanation can be given to describe the difference between the two methods. The determination of Henry's constant at infinite dilution (low vapour injection, symmetrical peak) by IGC gives the slope at the very beginning of the sorption isotherm, while the headspace method gives the slope later in the sorption isotherm graph assuming that the system is at infinite dilution without any control.

4. Conclusions

The goals of this preliminary study on the characterization of the cotton surface and cotton–fragrance interactions were not only to explore the potential of IGC to provide thermodynamic data quicker than headspace methods, but also to understand better the adsorption mechanism of certain molecules on textiles under ambient conditions. The results obtained by IGC show how it can be used to characterize the surface of the textile in terms of dispersive and specific components of the surface energy. Thermodynamic data such as enthalpy, entropy and Henry's constant allow us to analyse the physico-chemical affinity of fragrance molecules for textiles. This work opens the door to more investigations on cotton

(influence of the origin, industrial treatments, pigments, etc.), and also an extension to synthetic textiles, hair and their interactions with water and fragrance molecules.

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