



Characterisation of the surface of a cellulosic multi-purpose office paper by inverse gas chromatography

J.M.R.C.A. Santos^{1,3,4}, M.H. Gil¹, A. Portugal¹ & J.T. Guthrie²

¹Department of Chemical Engineering, FCTUC, University of Coimbra, 3030-290 Coimbra, Portugal

²Department of Colour Chemistry, The University of Leeds, Woodhouse Lane, Leeds, West Yorkshire, LS2 9JT, United Kingdom

³Present Address: Department of Colour Chemistry, The University of Leeds, Woodhouse Lane, Leeds, West Yorkshire, LS2 9JT, United Kingdom (Tel.: 0044 (0) 113 233 2809; Fax: 0044 (0) 113 233 2947; E-mail: ccdjmrs@leeds.ac.uk)

⁴Author for correspondence (E-mail: ccdjmrs@leeds.ac.uk)

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Abstract

The surface of multi-purpose cellulosic office paper has been analysed by inverse gas chromatography (IGC). The parameters determined were the dispersive component of the surface free energy, the enthalpy of adsorption and the entropy of adsorption of polar and apolar probes, the Lewis acidity constant, K_a , and the Lewis basicity constant, K_b . It can be concluded that the dispersive component of the surface free energy, γ_s^d decreases with temperature, in the range 50–90°C. The temperature coefficient of γ_s^d , $d\gamma_s^d/dT$, is $-0.35 \text{ mJm}^{-2}\text{K}^{-1}$. The values of K_a and K_b were determined to be 0.11 ± 0.011 and 0.94 ± 0.211 , respectively. The predominant surface basicity agrees with expectation, bearing in mind the presence of calcium carbonate, and of a styrene-acrylic copolymer, in the surface sizing formulation. It is thought that during the drying stages following the surface sizing treatment, the starch used as the binder migrates to the interior of the surface sizing layer and then to the paper bulk itself. This migration contributes to a decrease in the hydrophilicity of the surface, and also results in the surface showing only slight Lewis acidity.

Introduction

In order to optimise the retention of pigments/dyes/toner and, therefore, maximise the quality of the imaging process, (printing, photocopying, hand writing, and so on), two finishing treatments are used on the paper surface. These are surface sizing and coating. The main differences lie in the amount of solution used for the treatment of the surface. The type of paper analysed in this study had a surface treatment solution weight of less than 3 g/m^2 and, thus, is not considered to be coated. The paper was a multi-use substrate, intended for office work (photocopy, fax, laser printing, ink-jet printing and so on). In a sense, this study is part of the search for an 'universal' print-

ing paper that would be suitable for 'all' printing applications.

A sizing formulation usually consists of binder(s), pigment(s), and additives (optical brightener(s), anti-foaming agents, dispersant agents, etc). Examples of binders include starch, carboxymethylcellulose and poly(vinyl alcohol). Commonly used particulates include silica, precipitated calcium carbonate, titanium dioxide, aluminium oxide and coloured pigments.

The binders affect the penetration of liquids as they influence the hydrophobicity and the porous structure of the surface of paper. Furthermore, they improve the internal resistance, decreasing the release of fibrous material and dust, due to an improvement in the intermolecular forces between cellulosic fibres. The

interactions between pigments and binders also influence the porous structure of the surface, allowing for the control of the spreading and the penetration of liquids such as the ink-jet printing ink (Wagner *et al.*, 1996; Boylan, 1997; Garret & Lee, 1998). Moreover, they improve the opacity of the paper sheet.

Intermolecular forces between cellulose fibres and additives used in the production of paper sheets, ink-paper surface interactions occurring during printing and other interface phenomena, are determined by the nature and the properties of the surfaces of the compounds used (Kamdem & Riedl, 1992a; Riedl & Kamdem, 1992b; Belgacem, 1995; Chtourou *et al.*, 1995; Garnier & Glasser, 1996; Wagberg & Annergren, 1997). IGC has been used, with success, in studies concerning the aforementioned phenomena (Lee & Luner, 1989; Jacob & Berg, 1994; Belgacem, 1995; Chtourou *et al.*, 1995; Lundqvist *et al.*, 1995). The information obtained by IGC includes surface free energy, (dispersive and specific components), the surface acidic/basic character (K_a and K_b respectively, Lewis definition), the enthalpy of adsorption and the entropy of adsorption.

In this study, a commercial, multi-purpose office paper was analysed using IGC, as part of a project aiming a better understanding of the interactions between the components of ink-jet printing inks and the surface of the paper, together with the effect of such interactions on the ink-jet printing image quality. This paper concerns the determination of the dispersive component of the surface free energy, as determined by the interaction with a series of n-alkanes. The Lewis acidity/basicity of the surface was determined from the specific component of the adsorption energy of Lewis acidic probes and of Lewis basic probes.

Materials and methods

Materials

A commercial, multi-use office paper, Navigator[®], (produced in Portugal by Soporcel) was used as the substrate material. The ash content of this paper was 20% and the concentration of the internal sizing was 8 kg/tonne. The cellulosic fibres used in its manufacturing were 100% Kraft pulp fibres. The paper was characterized by having the total mass of 80 g/m². The surface sizing formulation contributed with 2.2 g/m² and consisted of: precipitated calcium carbonate (PCC), a styrene-acrylic copolymer, cationic starch

from potato origin and additives (optical brightener and anti-foaming agent).

In IGC analysis, analytical grade (Sigma-Aldrich Ltd) probes were used without further purification. The apolar probes were n-heptane, n-octane, n-nonane, n-decane and the polar probes were tetrahydrofuran (basic probe), acetone, diethyl ether, (amphoteric probes), chloroform and dichloromethane (acidic probes). Methane was used as a non-interacting reference probe.

Inverse gas chromatography

A Perkin Elmer 8400 Gc, equipped with a FID detector was used. The attenuation used was 2, with an offset of 5%. The GC was coupled to a Siemens Kompensograph X-T C1011 computing integrator/recorder. The detector and injector were heated at 130°C and the oven temperature varied between 50 and 90°C, in 10°C increments.

The inert gas used was helium (99.999 + % purity). The carrier gas flow rate varied between 0.50 and 1.33 cm³/s, during preliminary studies concerning the surface adsorption/bulk absorption of the probes used. The probe used in these studies was n-heptane. As no dependence of the free adsorption energy on the carrier gas flow rate was observed, bulk absorption was negligible and surface adsorption was the dominant probe retention phenomenon. This behaviour was consistent throughout a temperature variation. Therefore, the flow rate used for further studies was kept at approximately 1 cm³/s. The correction factor for pressure drops along the column was close to unity in all the experiments as the pressure drop approached the zero value. The flow rate was corrected for the temperature variation between the meter and the column.

The columns were cut from stainless steel tubing and shaped in a smooth 'U' shape to fit the detector/injector geometry of the instrument. The dimensions of the columns were 0.5 m length, with an outside and inside diameter of 6.4 and 4.4 mm, respectively. Before packing, the columns were cleaned with deionised water and acetone and dried at room temperature, for 1 day.

The column packing was prepared by cutting the paper into approximately 2 mm × 2 mm pieces. Prior to packing, the column was weighed. The stationary phase was introduced into the column under vacuum, small additions being made alternately to each end of the column. The column was then tapped gently

for several minutes to allow the support to achieve 'uniform' packing, following each addition of the stationary phase (paper). This procedure was continued until the column was filled to within approximately 6 mm of the ends. The stationary phase was then retained in the column by the introduction of small plugs of silanised wool. The column was then reweighed and the mass of support obtained by difference.

Probes were injected using a 10 μ l Hamilton syringe. The procedure consisted of inserting the syringe needle into the headspace of a vial containing the liquid probe. The syringe was then purged with air around 10 times and the remaining probe vapour was injected into the column.

The retention time was determined using the geometric technique outlined by Condor and Young (Kamdem & Riedl, 1992a). This is necessary due to the 'tailing' exhibited by some of the peaks obtained using polar probes. At least three separated determinations were used in averaging the retention time, data reproducibility throughout being better than 5%.

IGc data processing was carried out according to customary methods, well described in the literature (Chtourou *et al.*, 1995).

Results and discussion

Determination of the dispersive component of the surface free energy of the surface of the paper

In this study, the temperature was varied between 50 and 90°C, in increments of 10°C, in order to follow the change of the dispersive component of the surface tension, γ_s^d , with temperature and to evaluate the Lewis acid constant and the Lewis base constant, K_a and K_b , respectively, for the surface of the paper. The value of the net retention time, V_n , was calculated according to Equation (1)

$$V_n = (t_r - t_0).F. C. J. \quad (1)$$

Here, t_0 is the retention time of a non-interacting probe species, either air, or more commonly, methane; F is the carrier gas flow rate in cm^3/s ; J is a term that corrects for the compressibility of the carrier gas and C is a correction factor, allowing for the vapour pressure of the water at the temperature of the bubble flow meter used to determine the flow rate.

The net retention volume is related to the energy of adsorption through the following expression:

$$\Delta G_a = -RT \ln(V_n) + K. \quad (2)$$

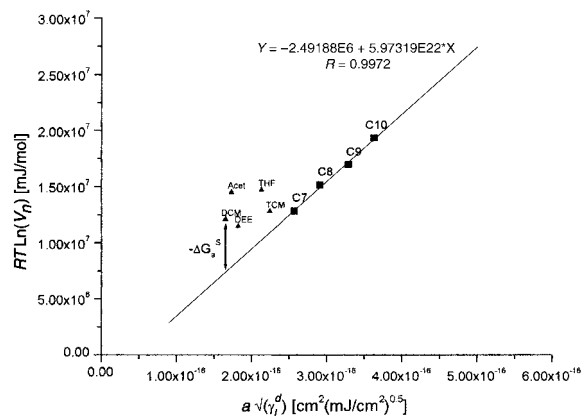


Figure 1. $RT \ln(V_n)$ versus $a\sqrt{\gamma_1^d}$ for n-alkanes and polar probes at $T = 50^\circ\text{C}$.

Here, ΔG_a is the free energy of adsorption, T the temperature, R the ideal gas constant and K is a constant related to the reference gas pressure and the reference surface pressure.

According to the Fowkes approach, the free energy of adsorption can be related with the surface tension of the solid through Equation (3)

$$RT \ln(V_n) = 2N_A a(\gamma_s^d)^{0.5}(\gamma_l^d)^{0.5} + K. \quad (3)$$

Here, N_A is Avogadro's constant, 'a' is the molecular surface area of the adsorbed species, γ_s^d and γ_l^d are the dispersive component of the surface free energy of the solid and the probe, respectively.

Figure 1, according to the Fowkes approach, contains a plot the free energy of adsorption against $a(\gamma_l^d)^{0.5}$, for the temperature of 50°C. Also represented is the free energy of adsorption, corresponding to the polar probes used. These probes were chosen for the determination of the specific component of the free energy of adsorption, $-\Delta G_a^s$, and K_a and K_b .

From the slope of the linear relation observed in Figure 1 it follows that the value of γ_s^d is $24.60 \pm 0.07 \text{ mJ}/\text{m}^2$, at 50°C. Following the same procedure, the values of γ_s^d at the temperatures of 60, 70, 80, and 90°C were determined.

Figure 2 shows that the dispersive component of the surface free energy decreases consistently with increase in the temperature. This decrease is an expression of an entropic contribution to the surface free energy. Similar values have been reported in other studies concerning cellulosic materials (Riedl & Kamdem, 1992b; Garnier & Glasser, 1994; Belgacem, 1995; Chtourou *et al.*, 1995;) and suberin (Cordeiro *et al.*, 1997). The temperature coefficient of γ_s^d , $d\gamma_s^d/dT$,

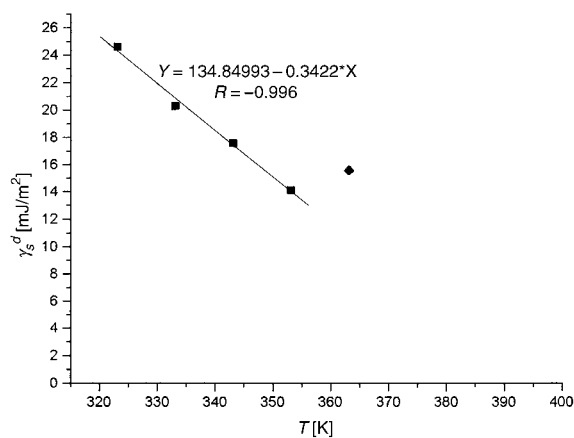


Figure 2. Values of γ_s^d at several temperatures.

is $-0.35 \text{ mJm}^{-2}\text{K}^{-1}$. This value for multi-purpose, cellulosic office paper can be compared to values obtained, for amorphous cellulose, of $-0.36 \text{ mJm}^{-2}\text{K}^{-1}$ in the range 50–100°C (Garnier & Glasser, 1994), for ‘pure’ cellulose, of $-0.21 \text{ mJm}^{-2}\text{K}^{-1}$, in the range -200 to 0°C ; of $-0.16 \text{ mJm}^{-2}\text{K}^{-1}$ for water at 20°C and of $-0.08 \text{ mJm}^{-2}\text{K}^{-1}$, for poly(methyl methacrylate), between 20 and 200°C (Riedl & Kamdem, 1992b). The value of $d\gamma_s^d/dT$ obtained in the present study is close to the results obtained by Garnier and Glasser, for amorphous cellulose. Nevertheless, bearing in mind the compounds used in the surface sizing formulation, mainly PCC, styrene-acrylic copolymer and cationic starch, it is difficult to assess which of these compounds is exerting the greater influence on the value of γ_s^d , and $d\gamma_s^d/dT$.

At 90°C (363.15 K), the value of γ_s^d is higher than one would expect considering the trend observed (Figure 2). This is thought to be due to the structural changes occurring at the surface of the paper, at that temperature. Bearing in mind the glass transition temperature of polystyrene ($\approx 100^\circ\text{C}$) and of polymethylmethacrylate ($\approx 105^\circ\text{C}$) (Stevens, 1990), and the porous structure of the surface of the paper, diffusion of the probe molecules into the interior of the surface sizing layer is thought to occur. Consequently, it was decided not to include the temperature of 90°C in the determination of the enthalpy of adsorption for the polar probes.

Determination of the enthalpy of adsorption and of the entropy of adsorption for the apolar probes on the surface of the paper substrate

The enthalpy of adsorption and the entropy of adsorption, of the probes used were calculated from the slope

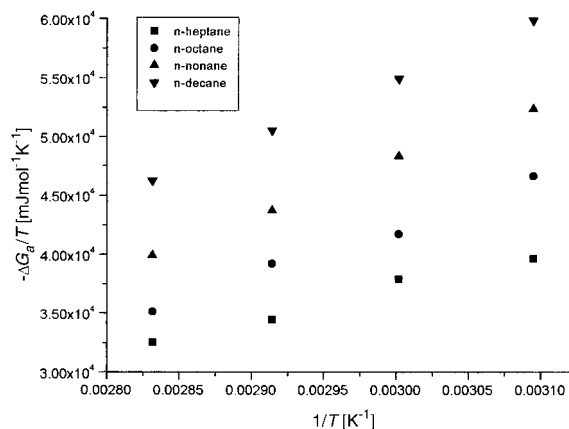


Figure 3. Determination of the enthalpy of adsorption and entropy of adsorption for n-alkanes on the surface of the paper substrate.

and intercept of $-\Delta G_a/T$ versus $1/T$, respectively, according to Equation (4)

$$\Delta G_a = \Delta H_a - T \Delta S_a. \quad (4)$$

Figure 3 illustrates the determination of the enthalpy and entropy of adsorption for n-heptane, n-octane, n-nonane and n-decane on the surface of the multi-purpose office paper.

The greater the value of $-\Delta H_a$, the greater is the interaction intensity between the probe molecule and the solid’s surface. Therefore, it can be concluded that the interaction intensity increases in the order: n heptane < n-octane < n-nonane < n-decane, as expected (Ohgushi & Umeno, 1987), and indicates a good performance of the column. The entropy of adsorption is lower than zero for all the n-alkanes, which agrees well with expectation as, during adsorption, the system goes from a less ordered phase (gas) to a more ordered adsorbed phase. The change in the entropy increases with increasing number of carbon atoms in the probes, again as expected.

Determination of the enthalpy of adsorption and the entropy of adsorption of polar probes on the surface of the paper substrate

The polar probes used were tetrahydrofuran (basic probe), acetone, diethyl ether, (amphoteric probes), chloroform and dichloromethane (acidic probes).

The value of the enthalpy of adsorption and entropy of adsorption were determined in the same manner as that used for the n-alkanes. The treatment is illustrated in Figures 4, 5 and 6. The values determined are given in Tables 3, 4 and 5.

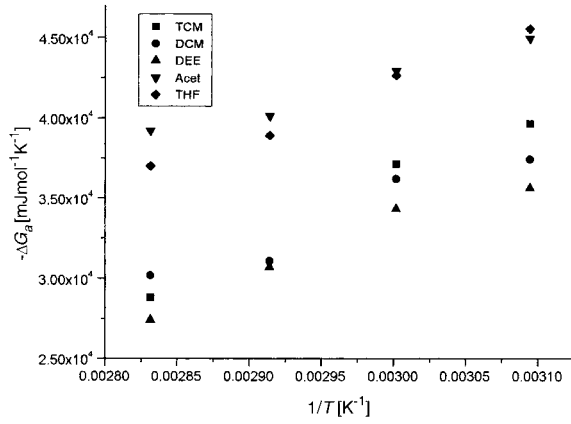


Figure 4. Determination of the enthalpy of adsorption and entropy of adsorption for the polar probes on the surface of the paper substrate.

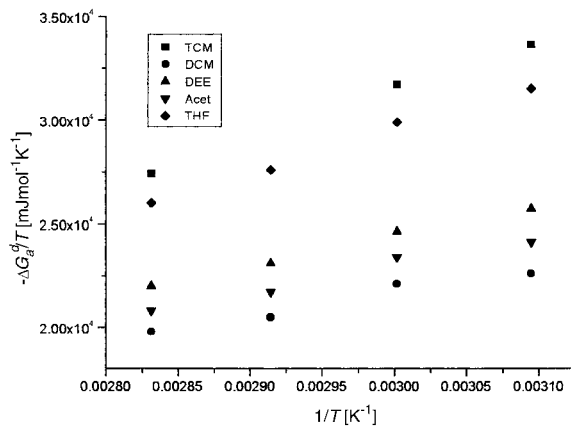


Figure 5. Determination of the dispersive component of the enthalpy of adsorption and entropy of adsorption for the polar probes on the surface of the paper substrate.

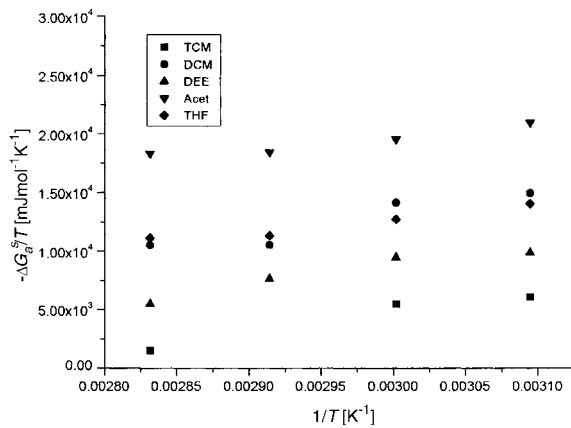


Figure 6. Determination of the specific component of the enthalpy of adsorption and entropy of adsorption for the polar probes on the surface of the paper substrate.

Table 1. Values of γ_s^d at several temperatures.

$T(^{\circ}\text{C})$	γ_s^d (mJ/m ²)	Correlation coefficient
50	24.6 ± 0.07	1.00
60	20.3 ± 0.12	0.99
70	17.6 ± 0.10	0.99
80	14.1 ± 0.23	0.98
90	15.6 ± 0.26	0.98

Table 2. Enthalpy of adsorption and entropy of adsorption for the n-alkanes on the surface of the paper substrate.

Probe	$-\Delta H_a$ (mJ/mol)	ΔS_a (mJ/molK)	Correlation coefficient
C7	$2.81\text{E} + 07$	$-4.70\text{E} + 04$	0.99
C8	$4.23\text{E} + 07$	$-8.45\text{E} + 04$	0.99
C9	$4.77\text{E} + 07$	$-9.50\text{E} + 04$	1.00
C10	$5.18\text{E} + 07$	$-1.01\text{E} + 05$	1.00

The value of the specific component of the energy of adsorption, $-\Delta G_a^s$, was determined by the method outlined in Figure 1, based on Equation (5):

$$\Delta G_a^{\text{tot}} - \Delta G_a^d + \Delta G_a^s. \quad (5)$$

Here, ΔG_a^d is the term representing the dispersive Lifshitz–van der Waals contribution to the total free energy of adsorption, ΔG_a^{tot} . ΔG_a^s represents the contribution to the free energy of adsorption by any Lewis donor-acceptor (specific) interactions.

Considering the enthalpy of adsorption, ΔH_a , as shown in Table 3, it can be concluded that the interaction intensity increases in the following order: Acet < DCM < DEE < THF < TCM. This behaviour can be understood bearing in mind the higher contribution of the dispersive forces to the total change in the surface free energy. This is as high as 95% for

Table 3. Enthalpy of adsorption and entropy of adsorption for the polar probes on the surface of the paper substrate.

Probe	$-\Delta H_a$ (mJ/mol)	ΔS_a (mJ/molK)	Correlation coefficient
TCM	$4.20\text{E} + 07$	$-8.97\text{E} + 4$	0.99
DCM	$3.04\text{E} + 07$	$-5.63\text{E} + 4$	0.95
DEE	$3.19\text{E} + 07$	$-6.25\text{E} + 4$	0.98
Acet	$2.29\text{E} + 07$	$-2.61\text{E} + 4$	0.99
THF	$3.31\text{E} + 07$	$-5.70\text{E} + 4$	0.99

Table 4. Dispersive component of the enthalpy of adsorption and entropy of adsorption for the polar probes on the surface of the paper substrate.

Probe	$-\Delta H_a^d$ (mJ/mol)	ΔS_a^d (mJ/molK)	Correlation coefficient
TCM	2.38E + 07	-4.00E + 04	1.00
DCM	1.13E + 07	-1.23E + 04	0.97
DEE	1.46E + 07	-1.95E + 04	1.00
Acet	1.30E + 07	-1.61E + 04	0.98
THF	2.16E + 07	-3.53E + 04	1.00

Table 5. Values of the specific component of the enthalpy and entropy of adsorption for polar probes on the surface of the paper substrate.

Probe	DN/AN^*	$-\Delta H_a^s$ (mJ/mol)	ΔS_a^s (mJ/molK)	Correlation coefficient	$-\Delta H_a^s/AN^*$
TCM	0.0	1.82E + 07	-4.98E + 04	0.97	0.804
DCM	0.0	1.91E + 07	-4.41E + 04	0.93	1.170
DEE	13.7	1.70E + 07	-4.21E + 04	0.96	2.892
Acet	6.8	1.36E + 07	-2.11E + 04	0.99	1.295
THF	40.2	1.15E + 07	-2.17E + 04	0.97	5.477

TCM at 80°C, the lower contribution being attributable to acetone, at around 53%, also at the temperature mentioned. This agrees with the suggestion of Fowkes and with experimental results (Ohgushi & Umeno, 1987). Therefore, the higher the value of $a(\gamma_i^d)^{0.5}$ for the probe, the higher should be the interaction intensity. The experimental data points confirm this interpretation as can be deduced from data presented in Table 3. The change in the entropy of adsorption, ΔS_a , follows a similar trend, increasing in the order: DCM < Acet < DEE < THF < TCM.

Accordingly, the trend of the dispersive component of the enthalpy of adsorption, ΔH_a^d , and of the entropy of adsorption, ΔS_a^d , follow a similar trend, increasing in the order: DCM < Acet < DEE < THF < TCM.

The specific component of the enthalpy of adsorption, as shown in Table 5, increases in the following order: THF < Acet < DEE < TCM < DCM. Thus, the intensity of the interaction between the surface and acidic probes, or amphoteric probes, is higher than for basic probes. Therefore, we can deduce that the surface of the multiuse office paper analysed is amphoteric, with a predominantly Lewis basicity. This observation can be confirmed by determining K_a and K_b . The fact that the strength of interaction with TCM

Table 6. Value for the surface area of selected polar probes (Chtourou *et al.*, 1995).

Probe molecule	a (nm ²)
THF	0.450
TCM	0.440
DCM	0.315
Acetone	0.425

is lower than with DCM, was not expected, as the value of AN^* is higher for the former. DN is equal to zero for both probe molecules. Nevertheless, taking into account the fact that TCM has the second higher surface area (Table 6), and the excellent correlation coefficient that is obtained for the specific component of the enthalpy of adsorption for this probe, one can attribute this behaviour to structural restrictions, which decrease the probability of establishment of intermolecular forces, of concern to accessibility to the most energetic sites on the surface (where these would be more probable).

Again, the entropy of adsorption is lower than zero for all the polar probes. The change in entropy follows a similar trend as that seen in the change

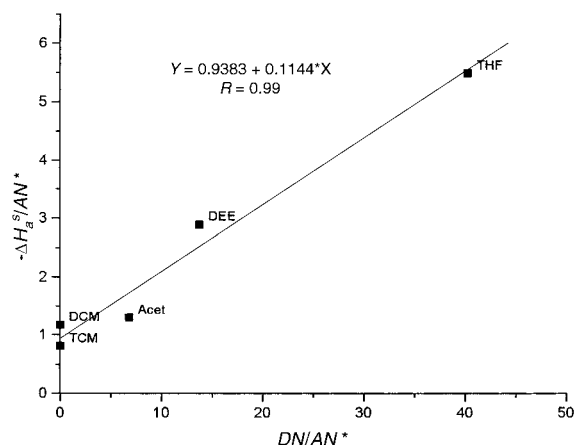


Figure 7. Determination of K_a and K_b for the surface of the paper substrate.

in enthalpy: Acet < THF < DEE < DCM < TCM, increasing with the strength of the interaction forces between the surface and the probe.

Determination of K_a and K_b

The values of K_a and K_b respectively were calculated using Equation (6) (Chtourou *et al.*, 1995):

$$-\Delta H_a = K_a \times DN + K_b \times AN^*. \quad (6)$$

Here DN and AN^* are Gutmann's donor and modified acceptor numbers, respectively, corresponding to the polar probes (Riddle & Fowkes, 1990; Kamdem, 1993). Representing $-\Delta H_a^s/AN^*$ versus DN/AN^* , one gets K_a as the slope and K_b as the intercept. The data are shown in Figure 7.

The linear regression for the data points in Figure 7 gives 0.11 ± 0.011 and 0.94 ± 0.211 for K_a and K_b respectively. This finding confirms the amphoteric, predominantly Lewis basic character of the surface of the cellulosic paper substrate.

As IGC was carried out at infinite dilution, the K_a and K_b determined relate to the Lewis acidity and Lewis basicity of the highest energy sites. These are the interaction sites that will interact preferentially with the acidic/basic sites of the components of an ink-jet ink, for instance.

The surface sizing formulation used in the treatment of the paper substrate contains calcium carbonate (to a large extent), a styrene-acrylic copolymer, a brightening agent, an antifoaming agent, and starch. It has been stated in the literature (Lundqvist *et al.*, 1995) that calcium carbonate is predominantly Lewis basic. The styrene-acrylic copolymer is hydrophobic

by nature. It has been proven (Gamier & Glasser, 1996) that the presence of the hydroxyl groups on the surface of cellulose is responsible for the predominantly Lewis acidic character of its surface. In a previous study, it has been proven that the surface of the multi-purpose office paper analysed is hydrophobic (the average value for the contact angle with water was 97°). This finding corresponds with the nature of the styrene-acrylic copolymer. Furthermore, if the concentration of the hydroxyl functional groups was high, the surface would be hydrophilic, and, therefore, the contact angle would be correspondingly lower than 90° .

The prevalent surface Lewis basicity is then justified by the surface low hydroxyl group concentration and by the presence of calcium carbonate and the styrene-acrylic copolymer. Any starch, used in the surface sizing formulation, is likely to have migrated to the bulk of the paper sheet and/or to the interface surface sizing layer-bulk of the paper, during surface treatment and the following drying stage (Yamazaki *et al.*, 1993). Thus, the starch at the surface would not be of as great an influence as that provided by the calcium carbonate or the copolymer, with respect to the surface Lewis acidic/basic properties.

Conclusions

The values determined for the dispersive component of the surface free energy decreased with increasing temperature, within the temperature range used. The temperature coefficient of γ_s^d , $d\gamma_s^d/dT$, is $-0.35 \text{ mJm}^{-2}\text{K}^{-1}$.

Considering the specific component of the enthalpy of adsorption, the interaction between the paper surface and the Lewis acidic probes, or amphoteric probes is stronger than with Lewis basic probe molecules. This is an indication of the amphoteric, predominantly Lewis basic, character of the surface. The values obtained for K_a and K_b , 0.11 ± 0.011 and 0.94 ± 0.211 , respectively, confirm this finding.

The predominant Lewis surface basicity is thought to be due to a low hydroxyl group availability, and to the presence of the calcium carbonate and the styrene-acrylic copolymer. The migration of the starch to the bulk of the paper sheet and/or to the interface formed by the surface sizing layer and the bulk of the paper, during surface sizing treatment (Yamazaki *et al.*, 1993), is thought to contribute to the lower surface Lewis acidity. A high hydroxyl functional groups

concentration would render the surface predominantly Lewis acidic and, therefore, hydrophilic.

IGC is useful in assessing and interpreting interactions between the paper surfaces, apolar probes and polar probe molecules. Such studies are of relevance to the analysis of the surface structure and chemical composition of cellulosic papers and their comparison. They are also of relevance to understanding the application properties of such materials, leading to their greater optimisation in service.

The interaction potential between the surface of paper substrates and pigments/dyes used in imaging processes can be assessed by determining the Lewis acidic/basic nature of the latter. This is of considerable importance when considering the optimisation of the imaging quality. Furthermore, a similar study concerning the major components and additives of a paper substrate would provide an understanding of the interactions occurring and, therefore, the final properties such as the efficiency of binding with the fillers that are used.

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