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SURFACE ENERGY CHARACTERIZATION OF SURFACE MODIFIED CELLULOSIC FIBRES BY INVERSE GAS CHROMATOGRAPHY (IGC)

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ABSTRACT

In the present study, the surface properties of cellulosic fibres have been systematically varied and the dispersive and acid-base properties have been determined by inverse gas chromatography (IGC) at infinite dilution.

Bleached kraft pulp fibres were carboxymethylated to different degrees. The results from the IGC measurements on the carboxymethylated fibres showed a linear relationship between the interaction energy with a basic probe (acidic properties) and the carboxylic acid group content. The extrapolation to zero degree of substitution of carboxylic acid groups indicates that, even in the absence of carboxylic groups, the fibres have acidic properties. The hydroxyl groups on

the fibres obviously also contribute to the acidic properties. The interaction energy with an acidic probe (basic properties) was relatively constant with increasing carboxylic acid group content. An increase in the degree of carboxymethylation also seemed to slightly increase the dispersive part of the surface free energy. This could be a consequence of an increase in electron density, a more compact structure after drying the carboxymethylated fibres or removal of low molecular weight impurities. The dispersive as well as the acid-base properties are approximately the same for pulps in both their proton and sodium forms.

The carboxymethylated fibres were peeled after the modification. The carboxylic group contents of the fibres and of the removed outer layers were determined by conductometric titration. The results showed that the carboxymethylation procedure is somewhat more effective in the outer layers of the fibres. IGC results for the peeled fibres pointed in the same direction.

Diethylaminoethyl (DEAE) cellulose, which has a basic functional group was also characterised. The IGC results showed that the DEAE cellulose interacts more strongly with the acidic probe than the reference cellulose material.

INTRODUCTION

The surface energy characteristics of cellulosic fibres are interesting during the papermaking process as well as in a number of end-use situations. For a better understanding of printing processes, especially for water-based printing, a better knowledge of the surface energetics is essential (1). The adhesion between toners and paper in electrostatic printing is also of great importance and is strongly influenced by the surface energy (2). It has long been known that the adhesion between paper and polyethylene in laminated products is influenced by the surface energies *cf.* (3).

The conventional and most direct method to determine surface energies of solids is by wetting measurements *i.e.* contact angle measurements. There are, however, some limitations in the use of wetting techniques to assess the surface energy of materials like paper and paper coatings. Depending on whether the contact angle is advancing or receding during the measurement, different contact angles can be observed. The hysteresis obtained can be due to several factors, such as surface roughness, surface heterogeneity, liquid absorption and the re-structuring of functional groups (4-7). Another limitation is the restriction on test liquids that can be used. When the surface energy of the solid is high, it is wetted by most liquids, *i.e.* the contact angle is 0 °.

A method which is not influenced by the surface roughness or absorbency of the investigated material is inverse gas chromatography (IGC) (8). Here, the material under study is the stationary phase in the chromatography column. The time or the volume of carrier gas required for the probe to pass through the column is a measure of the interaction between the probe gas and the column material. Inverse gas chromatography at infinite dilution has been successfully applied to determine the surface properties of various solids, including fibres and papers (9-12). Although IGC is a powerful technique for quantifying the surface energy properties, it has some disadvantages, *e.g.* the probe molar areas which are required to correctly quantify the acid-base interactions must be accurately known.

In the present study, we investigate the influence of chemical and mechanical surface modifications of cellulosic fibres on their surface energetics by studying their interaction with non-polar, acidic and basic probes. The experiments have not been performed at different temperatures to obtain the enthalpy of adsorption, ΔH, which means that we have not tried to characterise the acidic and basic properties by *e.g.* Gutmann donor and acceptor numbers. The use of this approach for complex surfaces such as those in the present investigation has often met with limited success, as illustrated in *e.g.* (13).

EXPERIMENTAL SECTION

Cellulosic fibres

The cellulosic fibres used for the carboxymethylation were from a fully bleached softwood kraft pulp (S-90, Mörrum, Södra Skogsägarna AB) which had been bleached only with ClO_2 (ECF-pulp). The pulp was washed with 0.01 M HCl to remove the metal ions followed by deionized water. The pulp was transferred to the sodium form by treatment with 1 mM $NaHCO_3$ and the addition of NaOH to pH 9. To remove excess electrolyte, the fibres were again washed with deionized water until the water surrounding the fibres had a conductivity less than 5 µS/cm. The fine material was removed using a Celleco filter with a 100 µm pore size. The charge density of the original fibres was 30 µeq/g fibre as determined by conductometric titration (14).

Diethylaminoethyl (DEAE) cellulose (Sigma Chemical Co, USA) is an anion exchange material made from high purity cotton linters. The DEAE cellulose had a charge density of 1.01 meq/g according to the manufacturer.

Carboxymethylation

The carboxymethylation procedure used is based on the procedure devised by (15). The method involves soaking a solvent-exchanged pulp in a solution of monochloroacetic acid in isopropanol and then transferring the pulp to a dilute alcoholic sodium hydroxide solution which has been heated to boiling. The amount of monochloroacetic acid added determines the carboxyl group content of the pulp, i.e. the degree of substitution. In this study, fibres were carboxymethylated to three different levels of substitution (DS = 0.018, 0.033, 0.048). After carboxymethylation, the pulps were washed and transferred to the sodium form following the same procedure as described above. A portion of the pulp with the highest carboxylic acid group content was also kept in the H^+-form for comparison.

Peeling procedure

The outer fibre cell wall layers P and S_1 were removed by hydromechanical peeling (16).

IGC MEASUREMENTS

Gas Chromatography Apparatus

A Varian GC 3400, equipped with a flame ionization detector (FID) of high sensitivity was used. The connections between column and detector were heated to avoid condensation of the probe gas on the sample. The injector was operated at 170°C, the column at 40 ± 0.1°C and the detector at 220°C. Nitrogen (N_2, 99.999 %) was used as the carrier gas. The flow rate of carrier gas was measured using a soap bubble flow meter and was corrected for pressure drops along the column and for the temperature variation between the meter and the column. The flow rate ranged from 10 to 20 ml/min for the different columns used.

Columns

Stainless steel columns, 5 mm in diameter and 0.6 m in length, were washed with ethanoic acid and dried before packing. Between 5.0 and 10.0 g of sample was packed into the columns. The samples were conditioned *in situ* in the column at 105°C overnight under a flow of nitrogen prior to measurement.

Probes

Alkanes ranging from *n*-hexane to *n*-nonane were used to determine the dispersive component of the surface free energy. The acid-base probe molecules used were dichloromethane (acid) and tetrahydrofuran (base). All probes were of analytical grade, (Aldrich, USA) and were stored in vials over molecular sieves. Table 1 presents the characteristics of the organic compounds chosen as the probes for the IGC experiments. The relevant characteristics of these probes are their molecular surface area, a, the dispersive component of their surface tension, γ^{LW} and their Lewis characteristics. The values given in Table 1 are from (17, 18). The probes were injected in the form of vapour, using a Hamilton CR-20 syringe and the probe volume was 0.05 to 5 µl. The small volume assured conditions near zero coverage. Each injection was repeated several times, showing that the elution peaks were reproducible. Methane was used to determine the gas hold-up time, t_{ref}, since it is non-adsorbing.

Probes	a (Å^2)	γ^{LW} (mJ/m^2)	Lewis charac-teristics
C_6H_{14}	51.5	18.4	Neutral
C_7H_{16}	57.0	20.1	Neutral
C_8H_{18}	62.8	21.6	Neutral
C_9H_{20}	68.9	22.9	Neutral
Tetrahydrofuran	45.0	27.4	Basic
CH_2Cl_2	31.5	27.6	Acidic

Table 1. Characteristics of probe molecules used in this work

Chromatographic Method

The measurements were performed at infinite dilution or zero surface coverage (Henry's law). This was confirmed by the fact that the resulting chromatograms were symmetrical, which is indicative of linear chromatography (19). Further verification that the results refer to the Henry's law region was obtained by varying the amount of the sample injected, and noting that the retention volume remained constant (20). The relative retention volume, V_N, is defined as the amount of carrier gas required to elute a given amount of adsorbate from the column. It is calculated from the following equation (19):

$$V_N = jF_{col}(t_R - t_{ref}) \tag{1}$$

where

$$j = \frac{3}{2}\left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}\right]$$

and

$$F_{col} = F_{meas}T(1 - p_{H_2O}/p_o)/T_{room}$$

where j is the James-Martin correction factor for gas compressibility; F_{col} is the corrected nitrogen flow rate; t_R is the retention time of the gaseous probe molecule; p_i is the inlet pressure of the carrier gas (atm); p_o is the outlet pressure of the carrier gas (atm); F_{meas} is the flow rate of the carrier gas measured at room temperature after the column outlet; p_{H_2O} is the water vapour pressure at the temperature of the chromatographic column T(K); and T_{room} is the room temperature (K).

When extremely low amounts of adsorbate are injected, the interaction between the adsorbed molecules can be neglected. The following thermodynamic relationship can then be applied to determine γ_S^{LW}, the dispersive component of the surface energy of the adsorbent, from V_N (21):

$$RT \ln V_N = 2a_{mol}\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + C \tag{2}$$

where R is the gas constant, a_{mol} is the molar area of the adsorbate on the surface, γ_L^{LW} is the dispersive component of the surface energy of the adsorbate, and C is a constant depending on the total substrate area and on the standard state chosen.

As n-alkanes are used as adsorbates, the interactions are due only to dispersive forces; hence, $RT \ln V_N$ is a linear function of $a_{mol}\sqrt{\gamma_L^{LW}}$. According to equation (2), γ_S^{LW} of the adsorbent can be calculated from the slope of this "reference line".

Deviations of V_N from the reference line occur when probes capable of interacting with the solid sample by non-dispersive, *i.e.* acid-base forces, are injected. The acid-base work of adhesion, W_a^{AB}, is (22) given by:

$$W_a^{AB} = \frac{RT}{a_{mol}} \ln \frac{V_N}{V_N^{alkane}} \tag{3}$$

The elution curves were symmetrical for all probes in this investigation, and the retention time is estimated from the time to reach the peak maximum.

At the column temperature used, 40 °C, surface adsorption on the cellulosic fibres is the only mode of probe retention. There is no penetration of the probes into the bulk of the fibres (23).

RESULTS

Conductometric titration of the fibres

The carboxylic acid group contents of the peel, the unpeeled and the peeled carboxymethylated fibres were determined by conductometric titration. The results are given in Table 2 and are also illustrated in Fig. 1. The charge density of the peel is somewhat higher than that of the unpeeled fibres. The peeled fibres show the same charge density as the unpeeled fibres. Even though the peel showed a somewhat higher charge density than the unpeeled fibre, this is the expected result since less then 5% of the total fibre volume was removed.

The results indicate that the carboxymethylation procedure is about 25% more effective in the outer part of the fibre.

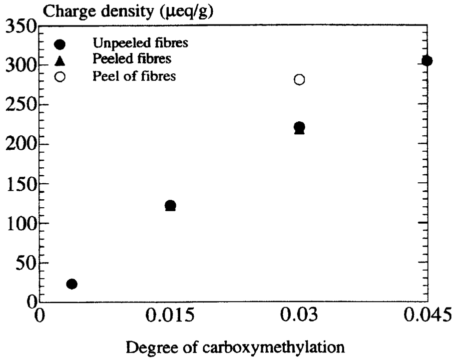

Figure 1. *The charge density for unmodified fibres and for the three levels of carboxymethylation. Unpeeled, peeled and peel.*

Fibre sample	Charge density, total (μeq/g)	Charge density, peeled fibres (μeq/g)	Charge density, peel (μeq/g)
Untreated	21-25		
I. DS = 0.018	121-123	121	
II. DS = 0.033	217-222	214-221	271-289
III. DS = 0.048	298-307	306-307	

Table 2. The charge density of the modified cellulosic fibres.

IGC measurements on fibres

IGC measurements on unpeeled carboxymethylated fibres

The specific surface areas of the carboxymethylated fibres, obtained from nitrogen adsorption isotherms by application of the BET equations are presented in Table 3. The values of the specific surface area were somewhat smaller than those reported by *e.g.* (24).

Column content	Sample weight, (g)	BET, specific area (m^2/g)*	Correlation coefficient	Sample area, (m^2)
Untreated	5.476	0.58	0.997	3.18
I. DS = 0.018	3.704	0.64	0.999	2.37
II. DS= 0.033	4.509	0.49	0.999	2.21
III. DS= 0.048	3.311	0.53	0.999	1.75

*Measurements performed at the Department for Engineering Chemistry at Chalmers University of Technology

Table 3. Column content, weight, specific area and total sample area.

Fig. 2 presents plots according to equation (2) for a homologous series of alkanes for the unmodified and the three systematically modified fibres. The level of the alkane line merely reflects the total sample area (Table 3). The dispersive parts of the surface free energy for the different fibres are shown in Table 4 and the results are presented in Fig 3. The values of the dispersive component of the surface free energy are in agreement with previous observations for highly purified cellulosic fibres (12, 21, 25, 26). A slight increase in the dispersive component of the surface free energy with increasing amount of carboxylic groups can be observed. The introduction of carboxylic groups increases the electron density in the structure. The carboxymethylated fibres are also more swollen and flexibilized and probably form a very compact structure when dried. The carboxymethylation procedure also involves an extensive washing of the fibres in an organic solvent which can remove any low-energy hydrophobic material. All these factors can contribute to the increase in dispersive energy.

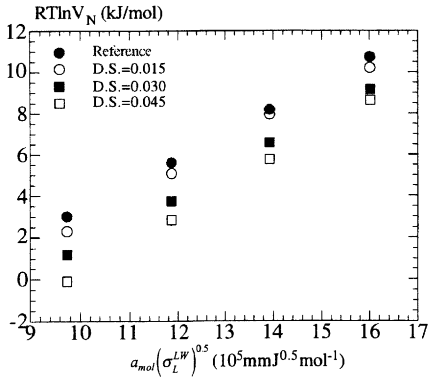

Figure 2. *Alkane lines for the reference and carboxymethylated cellulosic fibres at 40°C.*

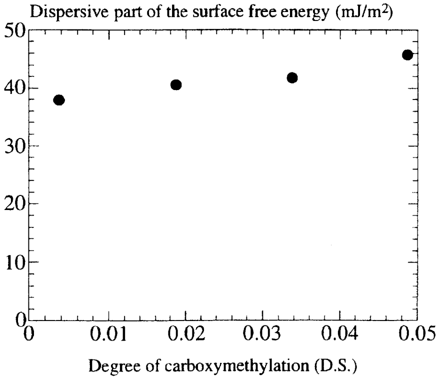

Figure 3. The influence of carboxylic group content on the dispersive part of the surface energy of the fibres at 40 °C.

The acid-base properties of the modified fibres were characterised using two polar probes: dichloromethane, an acidic probe, for the basic properties and tetrahydrofuran for the acidic properties. The interaction between the basic probe, tetrahydrofuran, and the fibres increases linearly with increasing carboxylic group content of the fibres as can be seen in Fig. 4. Since the pulps are in their Na^+-form, the acidic interaction is probably due to the Na^+-ions in the fibres. The intercept on the ordinate when the data are extrapolated to zero degree of substitution of carboxylic acid groups indicates that, even in the absence of carboxylic groups, the fibres have acidic properties (10 mJ/m^2). For the fibres with the largest degree of substitution the acidic interaction energy is 20 mJ/m^2. This result strongly implies that the hydroxyl groups contribute very significantly to the acidity of the fibre surfaces. It could be argued that the IGC method predominantly measures the high energy sites. It seems, however, very unlikely that the 5-fold increase in the content of carboxylic groups from untreated fibres to DS= 0.018 would give such a small increase in interaction energy if the interaction was dominated by the carboxyl groups.

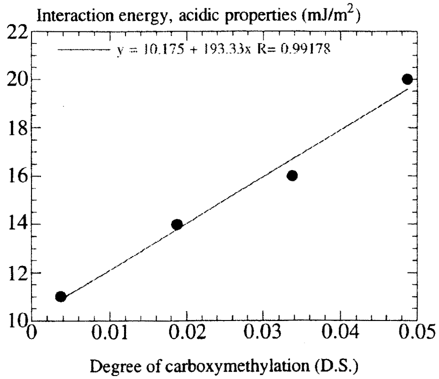

Figure 4 . *The influence of carboxylic group content on the acidic properties, interaction energy with a basic probe (THF) at 40°C.*

The interaction between the acidic probe, dichloromethane, and the fibres is relatively constant with increasing carboxylic group content, as shown in Fig. 5.

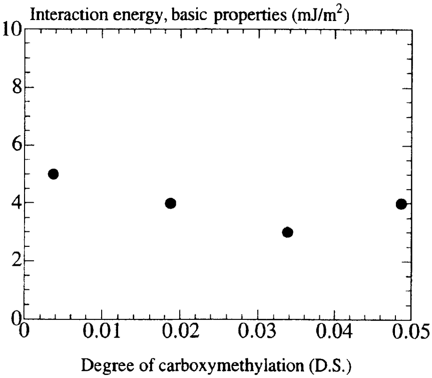

Figure 5. *The influence of carboxylic group content on the basic properties, interaction energy with an acidic probe (dichloromethane) at 40°C.*

The fibres with the highest carboxylic acid group content, DS= 0.048, were also characterised in their H^+-form. The results showed no significant differences between the dispersive and acid-base interactions and those of the same fibres in the Na^+-form, as is shown in Table 4. This obviously means that the acid-base properties are approximately the same for pulps in their Na^+- and H^+-forms, which is somewhat unexpected. It should however be pointed out that, in adhesion experiments, carboxylic groups in their proton and sodium forms in poly(ethylene butyl acrylate) (EBA) have given very similar adhesive strengths when laminated with cellophane (27).

Sample	Dispersive energy (mJ/m^2)	Acidic energy (mJ/m^2)	Basic energy (mJ/m^2)	Ionic form
Untreated	37.9	11	5	Na$^+$
I. DS= 0.018	40.5	14	4	Na$^+$
II. DS= 0.033	41.7	16	3	Na$^+$
III. DS= 0.048	45.7	20	4	Na$^+$
III. DS= 0.048 (peeled)	38.3	18	4	Na$^+$
III. DS= 0.048	44.9	20	4	H$^+$
DEAE cellulose	46.2	8	15	Cl$^-$

Table 4 The interaction energy with non-polar, basic and acidic probes for the unmodified and modified cellulosic fibres

IGC measurements on peeled carboxymethylated fibres

As can be seen in Table 4, the acidic properties were lower for the peeled fibres, but the basic properties were constant. These results agree with the results obtained from the conductometric titration of unpeeled and peeled fibres as well as of the peel. It seems that the carboxymethylation is more effective in the outer part of the fibre. The peeled carboxymethylated fibres with a degree of substitution of 0.048 showed a lower dispersive part of the surface energy than the unpeeled fibres. This result is somewhat unexpected but could be a consequence of the peeling procedure. During the long peeling procedure (~14 h) in water, the fibres may become contaminated with low surface energy material.

IGC measurements on diethylaminoethyl cellulose

Diethylaminoethyl (DEAE) cellulose was characterised with IGC to compare the acid-base properties with those of the carboxymethylated fibres. The results are shown in Table 4. The dispersive part of the surface free energy is similar to the values obtained by (12, 21) who obtained values from 45 to 50 mJ/m^2 for cotton cellulose. The interaction between the basic probe and the DEAE cellulose, the acidic part, is weaker than the interaction with the reference fibres. This is reasonable since cotton cellulose has less carboxylic acid groups than fully bleached kraft pulp fibres (28) and these groups may furthermore react during the derivatization of the cellulose. The basic interaction energy is on the other hand three to four times stronger than that of the reference fibres. The results for the carboxymethylated cellulosic fibres and the DEAE cellulose are compared with those for the reference cellulosic fibres in Fig. 6.

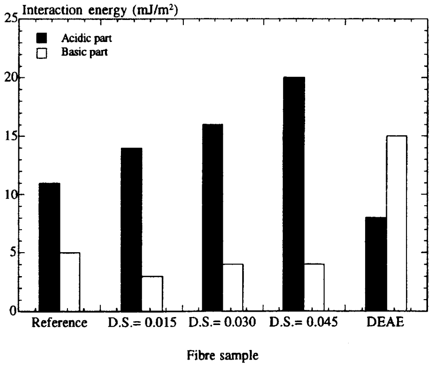

Figure 6. *The acid-base properties of chemically modified cellulosic fibres.*

CONCLUSIONS

The surface energetics of chemically and mechanically modified cellulosic fibres were characterised using inverse gas chromatography at infinite dilution. The degree of carboxymethylation of the fibres showed a linear relationship with the interaction energy with a basic probe (acidic part). The results show, however, that the carboxylic acid groups are not the only contributors to the acidic properties of the fibres. The hydroxyl groups on the fibres evidently also contribute to the acidic properties. The interaction energy with an acidic probe (basic part) was relatively constant when the carboxylic acid group content of the fibres was increased.

An increase in the degree of carboxymethylation seemed to increase the dispersive part of the surface energy slightly. This may be a consequence of an increase in electron density, a more compact structure after drying the carboxymethylated fibres or removal of low molecular weight impurities.

The dispersive as well as the acid-base properties were found to be approximately the same for pulps in their proton and sodium forms.

The conductometric titration and IGC measurements of unpeeled and peeled fibres and conductometric titration of the removed outer layers indicate that the carboxymethylation procedure is slightly more effective in the outer layers of the fibres.

The diethylaminoethyl (DEAE) cellulose which has a basic functional group showed a stronger interaction with the acidic probe than the reference cellulose material.

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Transcription of Discussion

Surface Energy Characterisation of Surface Modified Cellulosic Fibres by Inverse Gas Chromatography (IGC)

Lars Ödberg, Vice President, Basic Research, STFI, Sweden

Gil Garnier, Research Engineer, Paprican/McGill, Canada

I would like to ask two questions. The first one: most authors observe that with alkane probes you have Goussion, nice and symmetrical peaks. However, when you use an acid or a base probe, and especially when the degree of acidity or basicity increases, the peaks tend to become non-qaussian and exhibit important tailing. Have you observed such a phenomena?

Lars Ödberg

I can take that question first. All peaks for these bleached fibres were only slightly non qaussian. It wasn't really any problem. We made an evaluation both from the peak position and from the centre of gravity. There was only a small difference.

Gil Garnier

For your information, myself, Dr Gray, Dr Berg and Dr Gandini all observed the peak tailing phenomena and we believe that it could be related to the heterogeneity of the chemical sites. The second question: you used the Schultz-Lavielle approach to quantify the specific acid/base interactions. This gives only some relative information. How could you obtain absolute values?

Lars Ödberg

It is difficult to obtain absolute values. You have to make assumptions. For example, water is in one approach assumed to be just as basic as it is acidic. We think it is a better approach not to divide the non-polar surface energy into acidic and basic parts. You use the same probe all the time. We did this also with our experiment with coating layers and you can see if you change the coating layers and use a base probe the acidic properties of the coating layer changes.

Gil Garnier

How about using some surface force apparatus to be able to quantify that data and then relate the results to what you obtain by IGC with your specific probes?

Lars Ödberg

We haven't done that but it's perhaps a possibility.

Professor John Roberts, UMIST, UK

Your peeling work revealed homogeneous carboxymethylation throughout the fibre. Have you looked at different methods of carboxymethylation? This might lead to a heterogeneous distribution.

Lars Ödberg

No we haven't . We've only used this method by Walecka. You would like heterogeneous carboxylation in some instances and this is what Prof Ragauskas is going to talk about, where the carboxylic acid groups are introduced at the surface or in the bulk.

Bob Bates, Director PTD, Hercules European Research Centre BV, Netherlands

I have a question about your experimental protocol. Our studies on fibre show that even studies on relatively pure fibres contain small quantities but a very large number of volatile organic chemicals. How do you cope with that situation in your work?

Lars Ödberg

These fibres are conditioned in the GC column at 105°C overnight under nitrogen flow. I think that would take care of most of the volatile material in the fibres.

Steve Keller, Assistant Professor, Syracuse University, USA

I have a question about the BET surface areas that you determined to be about 0.6m^2/g. They seem low to me. There is another statement in the paper where you indicated that molecules were not penetrating the fibrous structure which, given typical time constants of interaction, at that temperature you would expect penetration of the probes deep into the pore structure. This is a concern that we had and you don't get it in calcium carbonate but how would you address that for the system that you studied?

Lars Ödberg

These fibres had no fines in them. We had taken away all of the fine materials using 100 micron screen. So even some fragments which are somewhat larger than fines have been taken away. That partly explains why we get so low a surface area. Please repeat the second question about penetration of the probes.

Steve Keller

IGC is based on gas-condensed phase interactions where the gas molecules freely penetrate the whole structure, much like nitrogen in a BET isotherm. One could expect that any structurous portion of that fibre that is open to the gas phase is also going to be accessible to the probe molecule. I would think that might explain the tailing coming off at the end of the IGC peak rather than heterogeneity in the surface energy. It has to do with the pore structure and how it affects your results.

Lars Ödberg

We see some tailing but not very serious. So whether that comes from heterogeneity of the sample or some part of the column being physically less accessible I can't say.

Bruce Lyne, Senior Manager, International Paper, USA

I guess we should ask ourselves why we want to know the acid base character of paper or fibres. In most cases it's to predict interaction of paper in a normal room atmosphere, or in the wet state if we are talking about fibres. So there is always bound water on the surface in any situation where we want to look at interactions. You have already alluded to the problems of IGC with respect to it being totally dry and there being no bound water present, but I also think that in the case of contact angle determinations using strong probes like THF and dichloromethane the probes displace the bound layer of water. What would the acid base character be like if you added back the bound water that you have under most conditions of interest?

Lars Ödberg

We have actually made experiments at 50% RH and we didn't see too much difference even in the acid-base part. It has been published in the literature that the dispersive part depends only slightly on the relative humidity. Derek Grey has made such experiments. We conditioned the sample at 50% RH for a long time but we didn't have the humidity well enough controlled during the experiment so we haven't published those results. It was a student summer work.

Gil Garnier

The beauty of IGC is that you can make the assumption that the coefficient of activity is equal to 1 and therefore you have a very clean, and nicely defined thermodynamics problem. However, as you increase the relative humidity the validity of this hypothesis decreases and if you go to inverse liquid chromatography it totally vanishes. How do you plan to deal with that?

Lars Ödberg

Do you mean how we intend to deal with the non ideality in liquid chromatography?

Gil Garnier

How do you plan to develop the mathematics because now you must assume a coefficient of activity below 0.8 and so you cannot assume the perfect gas state anymore.

Lars Ödberg

Do you mean when we inject more of the probe molecules in the IGC or when we go to the liquid state?

Gil Garnier

If you go to the liquid state and you inject some liquid probe in a liquid eluent you will saturate your column and loose the validity of a second important hypothesis in your work; infinite dilution conditions.

Lars Ödberg

I am aware there are many problems when you go to a liquid phase chromatography. I think we will take a rather practical approach. One application would be for water based printing inks where you could use probes that are similar to the components in your printing ink and see if different types of fibres interacted in different way. I think it is difficult to have a very fundamental approach in this area.

Prof Per Stenius, Helsinki University, Finland

About 10 years ago at the Institute for Surface Chemistry, Anders Larsson[2] determined adsorption isotherms of acid and basic probes on fibres from a completely non polar solvent. In that case we could not compare directly with water and the probes were different from those used in IGC but the study also indicated that both acidic and basic probes interact strongly with the fibre surface. So the adsorption from solution agrees quantitatively with IGC.

Lars Ödberg

These were made from organic solvents. I think with inverse liquid chromatography the advantage is if we could do it from water solution.

Lars Wågberg, SCA Research AB, Sweden

If you use different liquids to determine contact angle you have to take care of the hydrodynamics of the spreading of the droplet and this has not often been done so people use glycerol as one liquid and will hence not measure the proper contact angle if the hydrodynamics have not been considered. Now we are getting to a question that I have

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[2] Larsson, A and Stenius, P: Sorption of small organic molecules by cellulose from hexane: Nordic Pulp & Paper Res J.: 2:87-91: 1987

asked you before but I haven't had a full answer yet. Have you measured any contact angles on these carboxymethylated fibres?

Lars Ödberg

No we haven't measured them, we should have done so but we did a comparison in the slide you showed (review) but that's not these fibres.

Professor Torbjorn Helle, Norwegian Institute of Technology, Norway

I think you mentioned that these were ECF pulps, have you looked at other pulps of this particular type?

Lars Ödberg

There is an article in TAPPI where we also investigated TCF pulps and you see a little difference especially in the acidic properties. They are a little higher. The changes we saw between ECF and TCF pulps was approximately what you would expect from the slope of the line for different degrees of carboxymethylation that I had in this presentation here.