SFGP 2007 - Investigation of a Novel Principle of Chemical Grafting for Modification of Cellulose Fibers

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Abstract

Natural cellulose fibres have been employed for packaging applications for a long time. Their use, however, has been hampered by their high hydrophilicity and their moisture sensitivity. It has, thus, been proposed to circumvent this problem through the hydrophobic modification of their surface thanks to the use of molecular grafting approaches.

In this work, we describe the use of a novel solvent-free chemical pathway for molecular grafting that we have coined chromatogenic chemistry. It involves a reaction between a solid substrate and a reagent which is in a vapour-liquid equilibrium and diffuses within the solid substrate through a mechanism of adsorption/desorption akin to gas chromatography.

Chromatogenic chemistry phenomenon has been studied and modelled through the extensive use of a new specific test, the Droplet Surface Migration Test. It involves the deposition upon a porous substrate of a small amount of reagent and in studying its subsequent migration and grafting. Whatman paper and various long chain acid chlorides were used for this modelling. The acid chloride carboxylic ends react with the external hydroxyl groups of cellulose fibres to give rise to the formation of long chain hydrophobic ester bonds. Upon immersion of the paper sheet in distilled water, a hydrophobic spot, extending well over the initial depot zone, could then be clearly visualized, allowing to follow conveniently the

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reagent migration and reaction. Grafting densities were performed by using the HPLC technique.

The results obtained through the use of this test allowed a better understanding of chromatogenic chemistry phenomenon and an identification of the main parameters which affect the process: the nature of the reagent, the temperature, the reaction time, the nature of the substrate, etc. We have more particularly shown that the diffusion and grafting yields were maximal for a specific temperature which increases with the boiling point and therefore with the chain length of the reagents. We have proposed that this temperature should correspond to a compromise between the diffusion and reactivity properties of the reagent, its evaporation and its degradation by hydrolysis.

1. INTRODUCTION

Cellulose-based paper and board products are extremely versatile in meeting societal needs because they are relatively inexpensive, biodegradable and easily recycled (Mohanty et al, 2000; Vallette and Choudens, 1992). Yet a notable barrier to more widespread use, has been the difficulty in conferring adequate water barrier properties without compromising these natural qualities. Because of their hydrophilic character and porous structure, the use of paper and paperboard as water barrier in packaging industry, requests, often, a coating with synthetic polymers (Morino 2000; Furuheim and Axelson, 2003; Zhang et al. 1999). Addition of these layers of polymer alters, however, the natural and biodegradable properties of these materials as well as their recyclability.

An answer to this problem may lie in the development of hydrophobic cellulose. Indeed the hydrophilic character of cellulose fibres is due to the presence of external hydroxyl groups. Their heterogeneous esterification with long chain fatty acids has, thus, been shown to give rise to hydrophobic cellulose with good water barrier properties. The synthesis of long chain fatty acid cellulose esters is an approach which has been known for a long time. As early as 1930, Nathansohn, described the esterification of textile tissues by immersing the tissue in a mixture of stearoyl anhydride dissolved in various solvents, and then submitting the tissue for several hours at a temperature varying between 70 and 100°C. In the last decades, a renewed interest on esterification of cellulose with long chain fatty acids was observed (Kwatra and Caruthers, 1992; Vaca Garcia et al., 2000; Freire et al., 2006).The determination of the degree of substitution of fatty acid cellulose esters was also extensively studied (Freire et al., 2005; Vaca-Garcia et al., 2001). All these methods of cellulose heterogeneous acylation are seriously hampered, however, from the point of view of industrial production, by the need of the reaction to take place in an organic solvent and by the need to displace the reaction by the removal of its by-products.

Chromatogenic chemistry has been proposed by Samain (1998) to solve this problem and to achieve heterogeneous acylation through the control of the diffusion properties of fatty acid chloride reagents and of their by-product, HCl. This reaction is occurring in solid gas conditions, akin to the diffusion conditions occurring in gas chromatography. This analogy was responsible for coining the "chromatogenic chemistry" terminology. In this paper, we would like to describe new advances in the theoretical understanding and the experimental validation of this new grafting process. Previous works on chromatogenic chemistry (Samain et al., 2000; De Paola et al., 2001) had focused on the direct application of reagents on the surface of running web materials through printing technologies such as flexography. Although these processes were found to be efficient, detailed analysis of the interaction mechanism between the reagents and the paper

substrate was difficult to achieve. Difficulties were encountered, due to the fact that the reaction proceeds at high speed, and because the reagents were diffusing into the depth of paper sheet, which is very small (100µm) and thus very uneasy to observe. We have found that this could be done, however, by implementing an experiment using a specific geometric configuration that allowed the straightforward observation and quantification of the phenomenon. Indeed, the work described in this paper is based upon the development of a new test, the Droplet Surface Migration Test (DSMT). Its use allowed us to begin to shred some light into the mechanisms of chromatogenic chemistry. In the DSMT, instead of moving into the depth of paper, the reagent moves radially upon the surface of the paper. It offers, thus, unique advantages for the investigation of chromatogenic chemistry mechanisms. It is notably simple to use in a laboratory setting and allows the clear distinction between the deposition step and the diffusion/ reaction phenomenon.

2. MATERIAL AND METHODS

2.1 Chemicals:

Palmitoyl chloride (C16) and stearoyl chloride (C18) were purchased from Aldrich Chemical Company. Behenoyl chloride (C22) was kindly provided by Isochem (SNPE group). Petroleum ether (100-140°C), extra-dry and ethanol free chloroform and other chemicals were of laboratory grade and purchased from Acros Organics Company. They were used without further purification.

2.2 Cellulose sample:

Cellulose used in this work was the Whatman filter paper n°2 purchased from VWR international. The samples were received in 46 x 57 cm sheets. The paper sheets were cut by hand into small pieces of 10x10 cm and dried in an oven for 24 h at 60° C to remove water.

2.3 Esterification reaction - the DSMT

The grafting of the fatty acid chlorides onto Whatman paper was studied through the extensive use of the Droplet Surface Migration Test (DSMT). This test involves the deposition of a droplet of a fatty acid chloride solution upon a piece of Whatman paper, followed by the observation of its migration and grafting after a development step.

Reagents were mixed with aprotic dry solvents in order to obtain solutions of known concentration (10, 15 and 20 % v/v). Petroleum ether was used here to

prepare solutions of C16 and C18 whereas the solubilization of C22 was realized in extra-dry, ethanol free, chloroform.

A calibrated droplet (0,5 µL) of these solutions was deposited on the surface of a Whatman paper sheet, using a capillary tube. The solutions impregnate the paper as a liquid (owing to its wettability compatibility and capillarity effects) on a very restricted area. After drying of the solvent, the reagent forms an initial spot of radius Ro (that is measurable, around 3mm), Figure 1. The paper sheet was then introduced in a controlled temperature and controlled air flow oven during a definite period of time. Under the influence of temperature, the fatty acid chloride is subjected to a diffusion mechanism while reacting with the hydroxyl groups of cellulose, resulting into the formation of a spot of hydrophobic cellulose. In order to quench the reaction, the paper sheet is immersed in ethanol, then dried and immersed in distilled water to reveal the hydrophobic spot. Its radius Rc, much larger than Ro, is easily measured with a ruler and the corresponding surface areas may then be plotted against the various parameters of the reaction (e.g. time, temperature, concentration of solution…). Each experimental value was the mean of 6 distinct trials done in the same conditions.
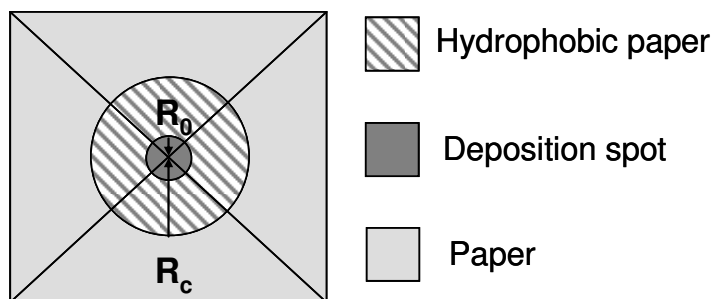

Figure 1. Scheme of the DSMT.

2.4 Determination of the grafted quantities by an HPLC analysis method

The analysis method of fatty acids that we developed, consisted in hydrolysing the grafted fatty acid in a basic medium, followed by neutralization, filtration and HPLC analysis of the free fatty. It allows the obtaining of quantitative data about the grafted quantities of fatty acid on the paper.

The hydrophobic spots, from which the initial surfaces of radius R_0 had been removed, were, first, introduced in a flask containing 25 ml of acetone. The mixture was stirred for 2h at room temperature in order to extract any unreacted fatty acid chloride and free fatty acid. After extraction, the pieces of paper were

removed from the flask and allowed to dry. An alkaline hydrolysis mixture (15 mL of a solution of ethanol KOH 0.2M and 10 mL of acetone) was added to the dry paper in a 30 mL well stoppered flask and kept at 60°C during 48 hours. The hydrolysis medium was then neutralized by addition of 0.256 mL of concentrated hydrochloric acid (36 %, 11.7 M). A precipitate of KCl was observed. The sample was then filtered using a PTFE syringe filter (Membrane filter - 0.45 μm) before its injection in the HPLC system.

HPLC from Dionex with an Interchrom Nucleosil N5C18-25 QS, 5 µm, 250 x 4,6 mm column and a pump model P680 which delivered a mixture methanol /1% acetic acid (v/v) at a constant rate of 1 mL/min was used. Detection was performed using a Eurosep DDL31 light diffusion detector with an air pressure of 1 bar, a nebulization temperature of 30°C and an evaporation temperature of 40°C.

Column calibration was performed via broad standard calibration procedure using the equivalent fatty acids in solution in the hydrolysis mixture at different concentrations. A reliable calibration curve was obtained for each fatty acid by the measurement of a series of 5 standards. These curves allowed the determination of the concentration of an unknown sample.

3. RESULTS

3.1 Influence of the reaction time

In order to study the effect of the reaction time on the surface of the hydrophobic spot, identical amounts of reagent were deposited on the paper and the reaction was allowed to proceed at different temperatures during 1, 5, 10, 15 and 30 minutes. The results obtained for 0.5 µl droplet deposition of a 10% palmitoyle chloride solution are presented on the Figure 2. They indicate, clearly, an initial increase of the surface area with time followed by a plateau. The value of this plateau, which is strongly dependent upon the temperature, and the time needed to reach it, decreases as the temperature increases. The kinetics of this phenomenon of diffusion/reaction is then clearly a function of the temperature. Furthermore, the maximum surface increases with the temperature, suggesting that the yield of the reaction is also dependent upon the temperature. This last observation indicates that the actual reaction mechanism must involve the interaction of complex phenomena and could not be described, with enough accuracy, through a conventional kinetic study and the determination of a kinetic constant.
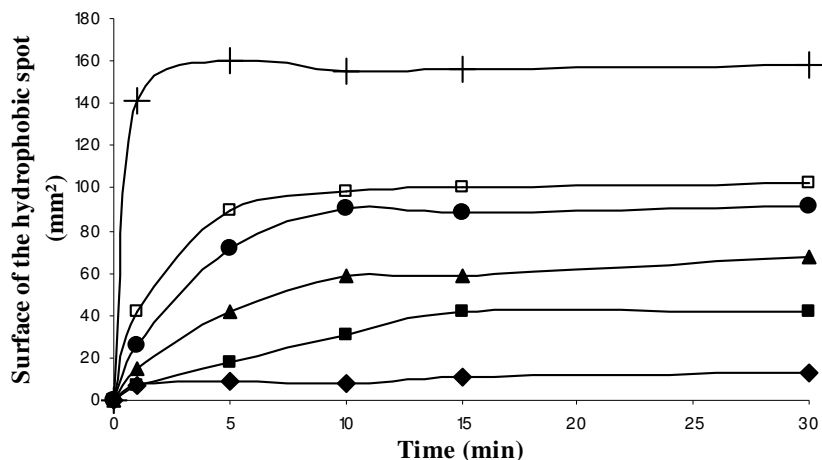
Figure 2. Surface areas of the hydrophobic spots versus reaction time at 50°C
(♦), 75°C (■), 90°C(▲), 100°C (•), 110°C (□), 140°C (+).

3.2 Influence of the temperature upon the final surface area of the hydrophobic spot

In this experiment, a constant amount of palmitoyl chloride (0,075 µl) is deposited upon the sheet of paper through the solvent droplet technique and the reaction is allowed to proceed long enough so that the maximum surface area for the hydrophobic spot could be attained. The results obtained for this reagent at different temperatures are presented on Figure 3. The area of the hydrophobic spots is strongly influenced by the temperature. At low temperature, almost no diffusion is observed, and then, as the temperature increases, we observed a sharp quasi-exponential increase in the surface area followed by a levelling off and eventually by a decrease.
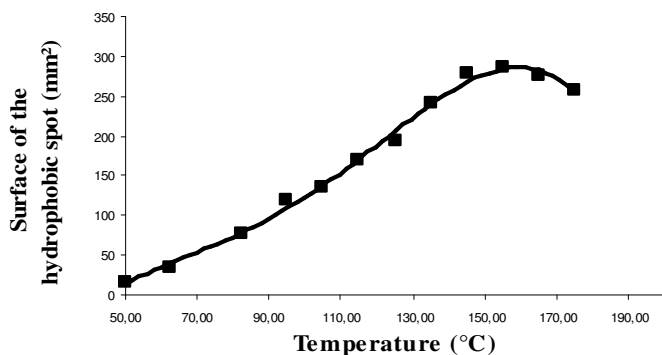

Figure 3: Surface areas of the hydrophobic spots versus temperature after deposition of a 0.5µl droplet of a 15% solution of C16

3.3 Influence of the chain length of the reagent upon the final surface area of the hydrophobic spot

The maximum surface areas for the hydrophobic spot for fatty acid chlorides having different chain lengths are plotted as a function of the temperature, as shown in Figure 4. Striking differences are observed between the curves corresponding to the different reagents. The general behaviour is however identical, but for different temperature ranges. The results obtained, indicated also that the surface area of the hydrophobic spot is clearly dependent upon the nature of the reagent and its chain length. Larger surface areas are observed with the C16 which is the shortest chain reagent. C16 also reaches its maximum value at lower temperature than the other two, notably the C22. These results seem to indicate that there is a strong relationship between the surface area of the hydrophobic spot and the diffusion capability of the reagents, which is connected to their vapour pressure, which is probably the driving force of a gaseous diffusion phenomenon.
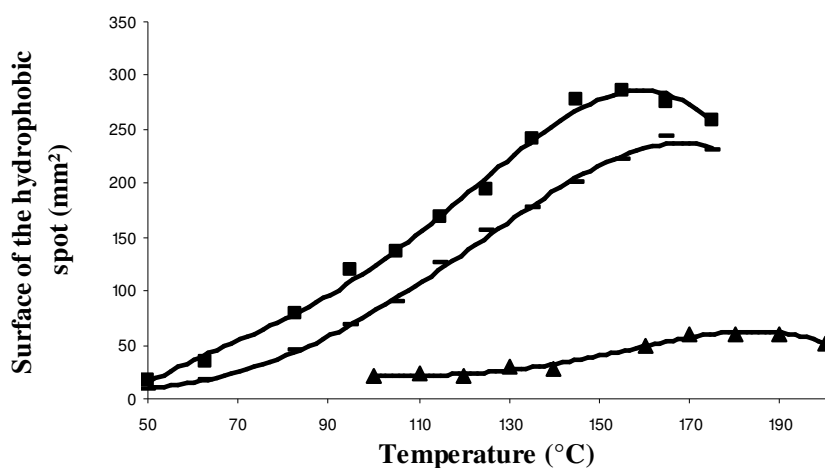

Figure 4: Surface areas of the hydrophobic spots vs temperature after deposition of a 0.5µl droplet of a 15% solution of C16 (■), C18 (─) and C22 (▲)

3.4 Measure of the density of the grafting

In the previous experiments (Figure 4), the amount of reagent deposited on the paper was a constant and equal to 0,075 µL (15% solution deposited droplet). Analysis of the results indicates clearly that large differences in the surface areas were observed even though the reaction was allowed to proceed to completion. Indeed smaller surface areas were observed for lower temperatures and larger surface areas for higher temperatures. We were then wondering whether these

large differences could be attributed to a higher grafting density at lower temperature.

In order to investigate this issue, we painstakingly proceeded to determine the grafting density of the fatty acid through an HPLC analysis of the amount of fatty acid present in the diffusion zone and covalently bound to the paper as it was mentioned in the experimental part. The results for the 10%, solution, expressed in amount of fatty acid grafted per square meter of paper, are presented in Figure 5. They indicate that, indeed, in our conditions, the grafting density has a constant value for a given reagent, and is completely independent of the temperature. The grafting density is, however, strongly dependent upon the chain length, with a higher density observed with the longer chain C18. This result is against conventional chemical wisdom in which increased chain length should give rise to larger steric hindrance and lower reactivity.
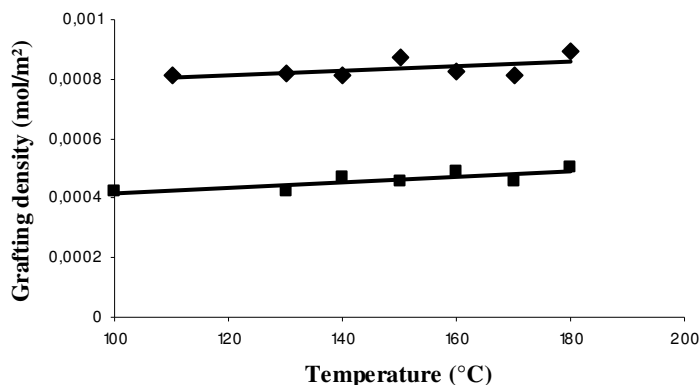

Figure 5. Density of the grafting versus temperature for a solution of 10% of C16 (■) and a solution of 10% of C18 (♦).

3.5 Determination of the yield of the reaction

The experimental work performed above has been done in order to measure the grafting density, but it is also straightforward to use it to measure the yield of the reaction because it provide access to the amount of fatty acid which has reacted with the paper. Comparison between this amount and the amount of reagent deposited gives the yield of the reaction.

The results obtained are presented in Figure 6. They indicate that the yield of the reaction is strongly dependent of the temperature reaching a 75% maximum at 170°C for the C18, and a 50% maximum at 160°C for the C16. These good results are unexpected given the way the reactions were done and given the extent of the diffusion process. The large difference between the C18 and the C16 is noteworthy. This indicates that careful optimization of the reaction, notably, by

controlling the chain length and the temperature could lead to nearly quantitative results.
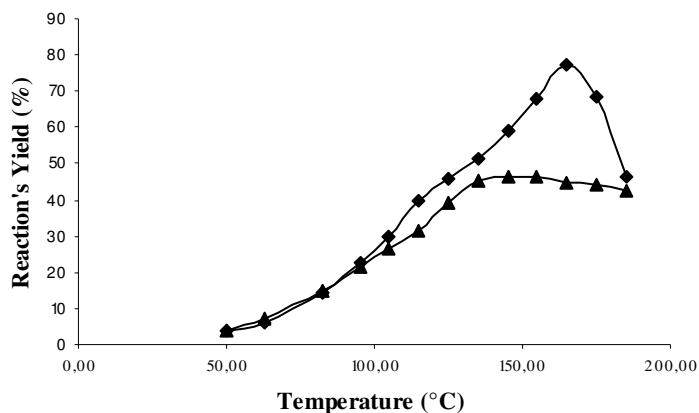

Figure 6: Yield of the reaction for solutions of C16-10% (▲) and C18-10% (♦).

3.6 Influence of the amounts of reagent deposited

In order to study the impact of the amount of reagent, we decided first to proceed to the comparison between the surface areas observed with the deposition of a 10% solution and the surface areas observed with the deposition of a 15% solution. The results obtained are presented in Figure 7 for C16 and in Figure 8 for C18. A strict 1,5 proportionality factor is observed between the two series of experiment, in the whole temperature range investigated for C16, and only slightly lower for the C18.
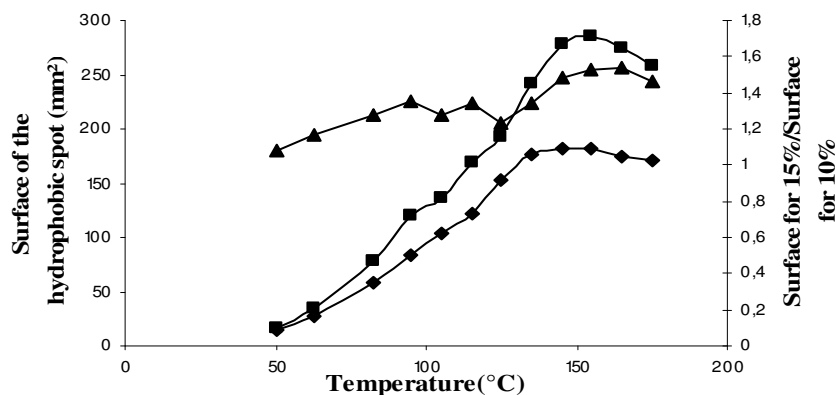

Figure 7: Surface areas of the hydrophobic spots for 0.5μl droplet deposition of solution of 10% (♦) and 15% (■) of C16 and ratio between these two surface areas: $S_{15\%}/S_{10\%}$ (▲).

Figure 8: Surface areas of the hydrophobic spots for 0.5µl droplet deposition of solution of 10% (♦) and 15% (■) of C18 and ratio between these two surface areas: $S_{15\%}/S_{10\%}$ (▲).
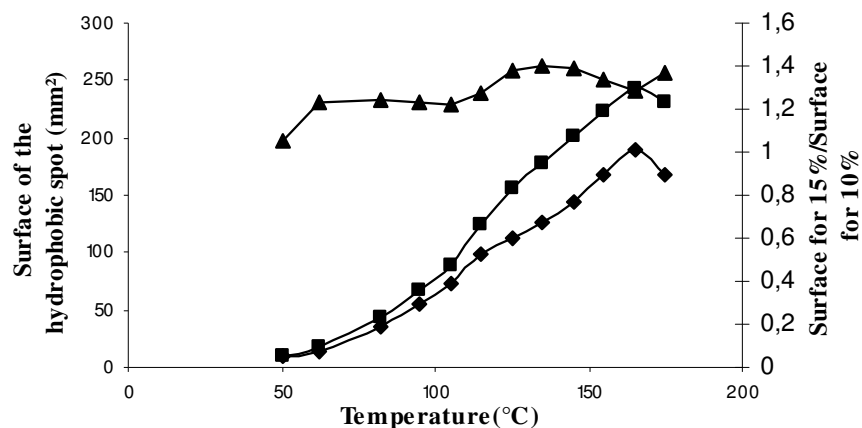
To go further in this line, we reasoned that, if the previous result was indeed accurate, then it should follow that the only explanation should be that the grafting density obtained with this type of chemistry is a constant depending only of the nature of the reagent and not of the quantity of reagent deposited.

To validate this hypothesis, we determined the grafting density of the amount of fatty acid grafted in the diffusion zone for the deposition of 0,05 µL and 0,075 µL for C16 and C18. The results are presented in Table 1 and confirm that the grafting density is not dependent of the concentration of the reagent.

Table 1. Density of grafting (amount of grafted fatty acids (mol) by surface area unit of paper (m²))

Concentration of reagent	10 %	15 %
Palmitoyl Chloride	0,000460	0,000473
Stearoyl Chloride	0,000815	0,000757

3.6 Qualitative experiments

The first qualitative result is provided by the visual aspect of the hydrophobic spots. They reproducibly exhibited a very sharp frontier between their hydrophobic and hydrophilic zones. This supports the idea that the grafting kinetic is very rapid in respect to the diffusion phenomenon. This implies that the progression of the sharp grafting front should be only governed by the rate of diffusion. The latter would be driven by the difference of concentration between the frontier of the initial liquid spot, where concentration of the reactant is at maximum, and the concentration at the outer frontier of the hydrophobic spot,

where it is almost zero, due to the very rapid chemical grafting. We can also suspect that this maximum reactant concentration is related to its vapour pressure.

We were also quite intrigued by the rather high yields of grafting that we had observed. This lead us to speculate, in a first approach, that the diffusion would occur mostly in the internal void volume of the paper, minimizing then the loss by evaporation of the reagent.

We thus designed a few simple qualitative experiments with the aim to validate or to infirm this hypothesis. In a first experiment, we drew a hole in the piece of paper, before applying the reagent, in the area where the diffusion should normally take place. In a second experiment, we deposited a thin bar of steel upon the surface of the paper, again in the area where the diffusion should take place. The results obtained were devoid of ambiguity. The hole in the paper did not prevent the diffusion of the reagent, while the steel bar did completely so. The results of these experiments were completely against the hypothesis of the reagent travelling only across the volume of the paper. Instead, the reagent seems to diffuse through the air phase along the surface of the paper, but remaining sufficiently close to the surface, because of its affinity with the substrate, and hence preventing its massive loss in the gas phase. This migration mechanism would resemble a conventional chromatographic migration mechanism, where the component affinity towards a solid support restricts the transport of this component. Nevertheless, these observations still need further understanding.

3.7 Discussion

The Clausius-Clapeyron's law, Equation (1), describes the relationship between the vapour pressure P_o, of a liquid as a function of temperature, and involving T_{eb}, the atmospheric boiling temperature of the component

$$P_o = P_{atm} \exp\left(\frac{\Delta H_{vap}}{R} \cdot \left(\frac{1}{T_{eb}} - \frac{1}{T}\right)\right) \tag{1}$$

Let us consider a product P with a boiling point at atmospheric pressure, T_{eb}, higher than T. According to Equation (1), even at temperature well below its boiling point, P is constantly in equilibrium between a liquid and a gaseous state. Because of the difference of concentration of the gaseous reagent on the surface of paper, a radial diffusion of P would take place. Thus, the surface of the porous substrate will be, progressively brought into intimate contact with the reagent P allowing it reacting and creating covalent bonds through the esterification reaction.

Equation (1) suggests that the diffusion can be increased by the use of a reagent with lower boiling point or by increasing the reaction temperature, as it

was illustrated by the Figure 4. Then, most of the results obtained could be interpreted satisfactorily considering the constant grafting density observed for each fatty acid coupled through Equation (1).

Still, we have to account for two, yet unexplained, phenomena: the decrease of the surface areas above a ceiling temperature, as can be seen on Figure 3, and the fact that the surface areas obtained at different temperatures, for the same amount of reagent, do not reach the same value over time, as shown on Figure 2. For the decrease of the hydrophobic surface areas above a ceiling temperature, we propose that an excessive increase of the reaction temperature or the use of a reagent with a lower boiling point could lead to a significant loss of reagent by evaporation (diffusion in the external air) lowering, in turn, the surface area of the hydrophobic spot.

For the fact that the surface areas obtained at different temperatures for the same amount of reagent do not reach the same value over time, we propose that the reagents, diffusing then at low speed, undergo enhanced degradation by hydrolysis inside the sheet of paper. Indeed, even after a drying step, paper materials are known to contain a significant residual amount of water which could damage the reagent in a timely fashion.

A consequence of these antagonist phenomena is the occurrence of an optimum temperature for the yield, as can be seen on Figure 5, where the yield of the reaction reaches a maximum for an optimal temperature which is specific for each reagent. This temperature is, in fact, a compromise between the diffusion, the reactivity of the reagent and two phenomena which are both prone to induce a loss of reagent: evaporation and hydrolysis.

An obvious prerequisite for any reaction to occur at the surface of a solid substrate is to get the reagent in contact with the reactive functions present at its surface. Conventional chemical wisdom argues that, in order to do just that, one would need an appropriate media with the ability to bring the reagents in close encounter with the surface of the substrate. These media are typically liquid solvents when the reagents are themselves liquid or soluble in liquids, or gaseous when the reagents are gaseous at the pressure and temperature conditions of the reaction.

From an industrial point of view, reactions performed in controlled gaseous environment are difficult and expensive to perform while the choice of solvent for reactions performed in liquid environment is extremely limited because of cost, safety and regulatory reasons.

In contrast, chromatogenic chemistry appears to be very efficient and straightforward. The amplitude of the diffusion phenomenon is quite large, and this indicates that it is possible to obtain a macroscopic uniform treatment while applying the reagent in a heterogeneous fashion. The only true processes requirements appear to be the control of the temperature and the necessity of

maintaining the right minimum amount of ventilation. The setting of this last parameter is indeed crucial since ventilation is necessary to ensure HCl removal, but too much ventilation would obviously be detrimental for the yield of the reaction. Note that this feature is indeed a beneficial consequence of the chromatogenic chemistry principle, in the sense that an undesired reactant, HCl, is displaced from the reacting zone, because of the very low value of its atmospheric boiling point, and that prevents the reverse reaction to occur. A similar principle has been already described by Schweich and Villermaux (Schweich and Villermaux, 1982) and was termed Chromatographic Reactor. In this case, a chemical reaction is operated in a packed column with sequential injection of reactants. Elution by the solvent, coupled with the different affinities of products in respect to the solid phase, allows differential migration and spatial separation of reagents and products, thus preventing undesired reactions to occur. In this way, Chromatogenic Chemistry could be regarded as operation of a Chromatographic Reactor.

4. CONCLUSION

In this paper, thanks to the elaboration of the novel DSMT protocol and to a fundamental approach, we have been able to successfully unveil some of the unusual characteristics of this technology. We have notably established the possibility of obtaining very high yields through the optimization of the grafting reaction and especially the temperature. As mentioned above, these optimal temperatures seem to be a compromise between the diffusion phenomenon, the reactivity of the reagent and its loss by evaporation and by hydrolysis. We have also shown that the grafting density is constant in the range of temperatures and concentrations investigated, while it appears strongly dependent upon the chain length of the fatty acid reagent.

Chromatogenic chemistry is a new technology but certainly has the potential to expand in the future as one suited for sustainable development (solvent free, eco conception, life cycle…). The fact that, given the tiny amount of reagent involved, we have been able to work with a closed oven, is certainly a key element for the high yields obtained and is probably foretelling for the optimization of future industrial conditions. Essentially, the chromatographic chemistry involves a chemical grafting of a solid phase, parasitized by a hydrolytic mechanism. These two chemical reactions are themselves intimately linked to mass transfer phenomena, i.e., a mechanism of diffusion-adsorption of the reactant along the paper surface, coupled with a loss of reactant by diffusion in the surrounding air. Such a complex configuration deserves a specific complex modelling that is currently in progress using the equation of radial diffusion with instantaneous chemical reaction.

Much remains yet to be done, however, to get a thorough understanding of this new brand of chemistry and of its true potential and we plan to report, soon, exiting new developments in this area.

NOTATION

ΔH_{vap}	Enthalpy of vaporization, J.mol^{-1}
P_{atm}	Atmospheric pressure, Pa
P_o	Vapor Pressure, Pa
R	Perfect gas constant, J.mol.K^{-1}
T	Temperature, K
T_{eb}	Boiling point of reagent, K

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