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A New Equation between Surface Tension and Solubility Parameters of Cellulose Derivatives depending on DS: Application on Cellulose Acetate

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Abstract

Generally, grafting alkylated chains onto cellulose backbone modifies its physicochemical properties strongly, and the variation in the hydrophobicity of the cellulose causes significant modifications of these superficial characteristics. In this sense, this study highlighted the effect of the hydrophobicity-hydrophilic balance brought by the level of grafting chains on the surface tension, and relationship between the surface tension measurements and the solubility parameters of activated surface. The results obtained from FTIR and ^{13}C NMR analysis confirmed the molecular structure of acetylated compounds with substitution occurring preferably at C-6, C-2 and C-3 hydroxyl positions, respectively. The surface active properties were investigated by the density of elaborated polymers and its relationship with the Parachors based on the Group Contribution Method. This study may help to increase the using natural and biodegradable fibers as surface-activity industrial materials. The calculations of Parachors (P) and densities of cellulose acetates samples (CA) at different substitution degree (DS) make to find a new relationship between the surface tension and the DS. These equations show that the surface tension variation depending on DS can be linearly or polynomial which explains that the surface tension of the cellulose acetate is highly depends on its DS.

1. Introduction

Thin polymeric films are largely used in many technological applications, as for instance, as coatings, paint, and sensors. Polymer surface energy and interface tension between substrate and polymeric film drive the stability of thin polymeric films. If the work of cohesion is larger than the work of adhesion, thin polymer film becomes unstable, resulting in the rewetting phenomena [1, 2]. Cellulose esters are frequently applied as binders, additives, film formers or modifiers in automotive, wood, plastic and leather coatings applications. However, grafting the new functionality on the cellulose backbone can modify some of its physicochemical properties (e.g. solubility) according to the DS of grafted alkylated chains [3]. The surface tension (γ) of the polymers in conjunction with other physicochemical parameters, including the solubility parameter (δ) was the subject of several studies [1, 2, 4, 5]. Moreover, industrial demands and environmental constraints impose and orient these studies focusing on biodegradable polymers and environmental friendly materials. In this area, the polysaccharides represent an important family, especially cellulose and its derivatives [6-10]. In this sense, several efforts have led to develop a considerable number of empirical equations describing the relationship between surface tension and solubility parameters [11]. We present below some equations describing the relationships existing between these parameters.

$$\gamma \approx 0.75 \,.\, e_{coh}^{2/3} = 0.75\, \delta^{4/3} V^{2/3} \quad (1)$$
$$\delta \approx V^{-2/3}\sqrt{\gamma} \quad (2)$$
$$\delta \approx 4.1\left(\gamma / V^{1/3}\right)^{0.43} \quad (3)$$
$$\gamma = 0.01707\ \delta^2 V^{1/3}, if\ n_{OH} + n_{COOH} + n_{aCOH} = 0 \quad (4)$$
$$\gamma = 0.0068\ \delta^2 V^{0.45} \quad (5)$$

Where γ is the surface tension, δ is the solubility parameter, Vis molar volume and e_{coh} is the cohesive energy.

However, cellulose and its derivatives represent an "exception" because of an important structural parameter "degree of substitution (DS)" which strongly influences its physicochemical properties such as solubility, thermal stability, etc. [3, 12, 13]. The analysis of the literature allows us to observe that the effect of the substitution degree is a good explanation for the diversity of the surface tension values of cellulose acetates. Table 1 shows the surface tension (γ) values of cellulose acetate cited in literature, a large difference between the values of the surface tension is noticed, and we suggest that this fluctuation is due to not taking into consideration the degree of substitution.

Table 1: Diversity of the surface tension values of cellulose acetate cited in literature

γ (mJ/m^2), 20°C	Ref.
38.2	[14]
45.9	[15]
40.3	[16]
38.0	[17]
52.6	[18]

Based on the geometric approach proposed by *P. Becher* [19] and the concept of solubility [20], we have shown that there is a strong relationship between the degree of substitution and geometric parameters (the surface to volume ratio) [21] and consequently between the DS and the surface tension. To understand and to control the process involved in the modification of cellulose derivatives products is of fundamental importance to optimize their uses. Besides, the final properties of materials produced from cellulose are heavily influenced by the distribution and values of DS, which are essentially dictated by crystallinity degree, molecular orientation, etc. At this moment, the relationship between the DS values of cellulose derivatives and their surface tension (γ) has scarcely been investigated.

The purpose of this work is three fold; firstly to perform material characterization in order to define optimal stocking and injection molding conditions. It is therefore compulsory in order to reach optimal material performances to define preconditioning procedures and processing windows. It can easily be understood that the physical properties of cellulose derivatives have to be well known to process them as conventional thermoplastic polymers. In this study, we highlight the hydrophobicity brought by acetyl groups on cellulose backbone by comparing its solubility and its interfacial properties with those of hydrophobically modified amount.

2. Materials and methods

2.1. Materials

Alfa “Stipa-tenacissima” cellulose fibers were dried in a vacuum oven at 90 °C for 48 h before their use for modifications. Toluene, Tetrahydrofurane and glacial acetic acid are purchased from Aldrich and dried before their uses. Acetic anhydride was used without any further purification. All other chemicals were of analytical grade and are used without further purifications and purchased also from Aldrich.

2.2. Methods

2.2.1. Isolation of cellulose from Esparto "Stipa-tenacissima" plant

Native Esparto "Stipa-tenacissima" fibers used in this work were purchased from Oriental (eastern) Morocco. Cellulose was extracted according to the procedure described by *El Barkany et al.* [22]. In summary fine particulate fibers were treated with a 1N NaOH solution at 80 °C for 2 h under mechanical stirring. This treatment was repeated three times, after each treatment, the fibers were filtered and washed with (NaClO), distilled water, ethanol and ether diethyl several times. The resulted fibers were dried under vacuum.

2.2.2. Preparation of Cellulose acetate with different DS

The starting cellulose acetate (DS~2.9) was prepared from Esparto "Stipa-tenacissima" cellulose fibers in toluene/acetic acid mixture, a catalytic amount of perchloric acid was added. 1 g of Esparto "*Stipa tenacissima*" cellulose fibers was activated for 1 min in toluene/acetic acid (10/5 ml: v/v) mixture, and 5 ml of acetic anhydride were added drop-wise into the reaction flask. The mixture was kept at room temperature under stirring for 15 min. the solution obtained was precipitated in distillated water, the precipitate was recuperated by filtration under vacuum, washed by distillated water and dried at constant weight at 40 °C and stayed one week in desiccators with P_2O_5.

2.2.3. Deacetylation of cellulose acetate

Cellulose triacetate (DS=2.9) was partially deacetylated to an appropriate degree of substitution and was evaluated by comparing surface tension measurements and solubility parameters evolution with hydrophobicity of substitution degree of cellulose acetate. The cellulose acetate samples at varying DS were prepared by the partial saponification reaction in KOH/Ethanol solution. Thus, the normality of KOH solution should be in accordance with the quantity of the hydroxyl groups (OH) wanted to deacetylate. e.g. to deacetylate one hydroxyl group (OH) of Anhydrous Glucose Unit (AGU): 1 g (3.58 mmol) of tri-O-acetyl cellulose (CA DS~2.9) was suspended in 50 ml of 7.16 10^{-2} N of KOH solution (0.2g/50ml of KOH/ethanol) (0.4 g/50 ml and 1 g/50 ml for deacetylating two and three groups respectively) in glass flask reactor equipped with mechanic stirring and reflux condenser. The deacetylation reaction was kept at room temperature for 24 h. Afterward, the mixture was filtered under vacuum and thoroughly washed with ethanol and ether diethyl, dried at 40°C then putted at room temperature in P_2O_5 desiccator

2.2.4. Determination of bulk density

Volumetric weight of the cellulose acetate samples is determined using a pycnometer, and it was calculated by Equation 6:

$$\rho_S = \rho_{H_2O} \cdot \frac{m_2 - m_1}{m_2 - m_3} \quad (6)$$

ρ_S is the volumetric weight of cellulose acetate, ρ_{H2O} is the volumetric weight of distilled water =1.005 g.cm^{-3}, $m_1$is the weight of the pycnometer filled with distilled water, m_2 is the weight of the pycnometer filled with distilled water + polymer, and m_3 is the weight of the pycnometer containing the polymer and distilled water.

3. Results and Discussion

Cellulose properties and attributes can be suited to different applications to create new materials readily available, renewable, and sustainable and thus they represent a natural resource of incredible importance. The development of methods for surface functionalization of cellulose can be expected to allow further control to attain supra-structures and highly hierarchical assemblies, etc. The impact of the acetylation content on the hydrophobic properties of cellulose films can be evaluated in terms of wetting characteristics and others properties. Surface tension values are another method to highlight the hydrophobicity brought by the alkylated chains. The cellulose acetate sample having a substitution degree value equal at 2.9 (DS~2.9) was prepared according to the following scheme (figure 1):

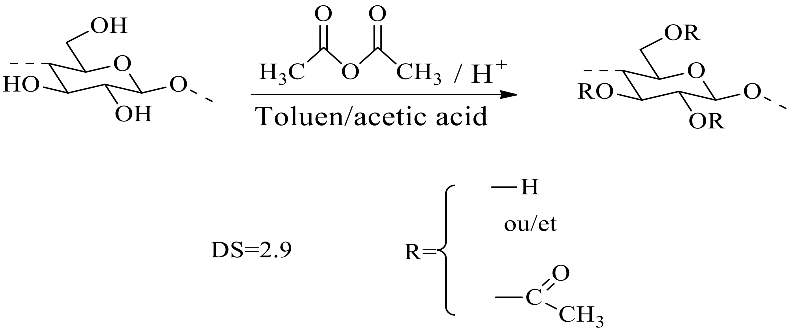

Figure 1: cellulose acetylating (DS~2.9)

3.1. *Spectral analysis*

3.1.1. FTIR

FTIR spectroscopy was used to investigate the chemical characteristics of the cellulose samples before and after the deacetylation. The exact ester content can be calculated after the FTIR calibration, where the average values are correlated with the ester contents of the standards and a linear relationship is obtained. The figure 2 shows the FTIR spectra of unmodified cellulose and cellulose acetates (DS≈1, 74 and DS≈2, 7).

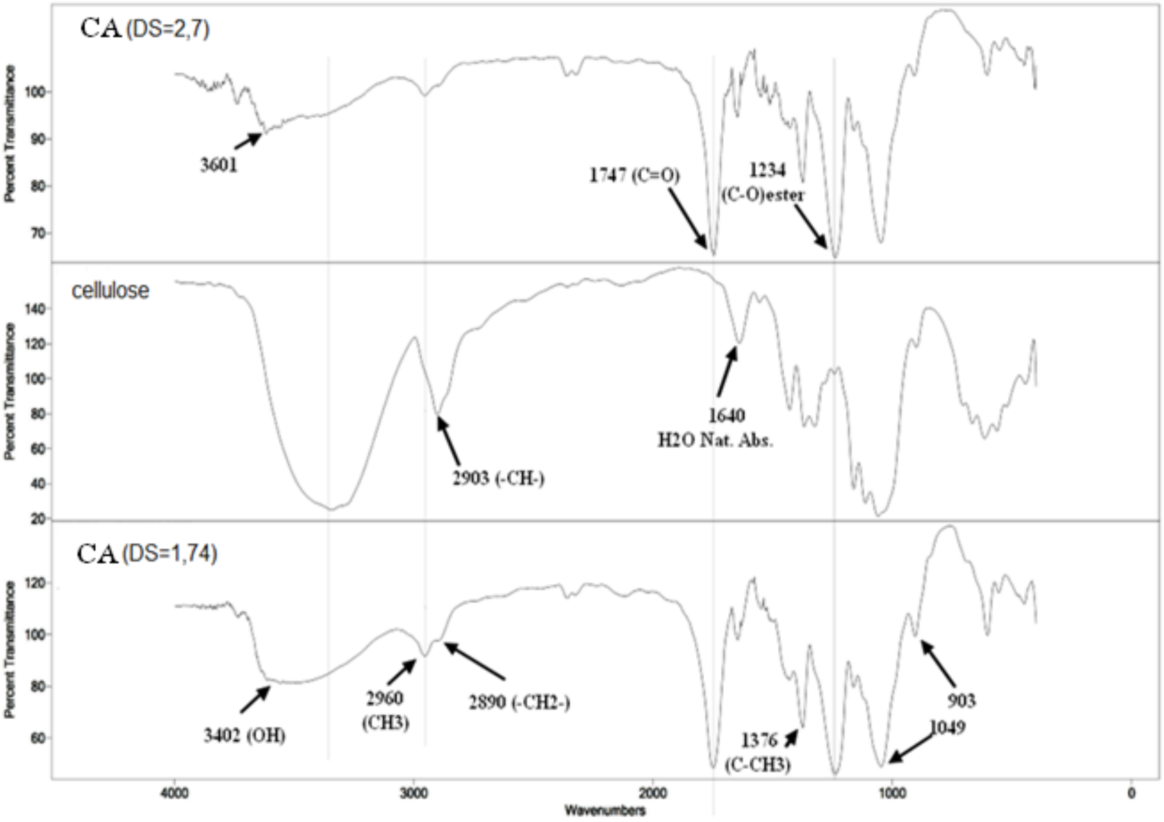

Figure 2: FTIR spectra of unmodified cellulose and cellulose acetates (DS1.74 and DS2.7)

The formation of cellulose acetates is proved by the reduction in the intensity of the characteristic absorption band of hydroxyl groups OH and the appearance of three new bands characteristic of acetyl groups: the high intensity of the absorption band characteristic of carbonyl ester (C=O)$_{ester}$ appeared at 1747 cm^{-1}, the band at 1376 cm^{-1} is attributed to the (C-CH$_3$) elongation and that around 1234 cm^{-1} is allocated to the elongation (C-O)$_{ester}$ [23, 24]. The absorption band observed at 1640 cm^{-1} corresponds to naturally absorbed water [25], the bands at 2960 cm^{-1}, 2890 cm^{-1} and 2903 cm^{-1} are associated respectively to the CH$_3$, CH$_2$ and CH elongation [26]. The absorption band around 1049 cm^{-1} is assigned to CO cyclic glucopyranose [27], and absorption band at 903 cm^{-1} is attributed to the β- glycosidic bonds situated between glucose units. The stable intensity of β-glycosidic absorption band indicates the non degradation of cellulose fibers during the modification reaction. As expected, the absence of any absorption bands in the region 1840-1760 cm^{-1} in the CA samples shows that the products are free of the unreacted acetic anhydride. Moreover, the lack of any peaks at 1700 cm^{-1} assigned to carboxylic groups indicates that the products are also free of the by-product of acetic acid.

3.1.2. NMR (^{1}H NMR and ^{13}C NMR)

The successful acetylating of cellulose was confirmed by examining the NMR spectra of unmodified and acetylated cellulose, and the results are shown in Figure 3. ^{1}H NMR and ^{13}C NMR analyses were used to evaluate the molecular structure and to elucidate the distribution of acetyl groups in cellulose acetate samples [28]. The results showed that strong signals within the chemical shift range from 1.8 to 2.2 ppm are attributed to methyl hydrogen of acetyl groups (Figure 3A). The protons of the cellulose backbone were located between 2.8 and 5.5 ppm. The distribution of the acetyl moiety among the three OH groups (C6–OH, C3–OH, C2–OH) in an AGU unit was evaluated roughly from the quantitative integration of acetyl methyl protons area of the ^{1}H NMR spectrum. It can be seen that the three hydroxyl groups at C2, C3, and C6 position exhibit different reaction activities, and the order of reactivity is C3–OH > C2–OH > C6–OH which is similar to the acetylation from those industrially synthesized through a heterogeneous acetylation hydrolysis process [29], and is different from those C6–OH > C2–OH > C3–OH, in ionic liquids [30] In Figure 3B, the signals within the chemical shift range 170 ppm assigned to carbonyl carbons were observed after the modification, which were consistent with the results in previous publications [30-32].

The peak at 62.0 ppm is assigned to the C6s carbon bearing a substituted acetyl group. However, the weak peak at 60.0 ppm is assigned to the unmodified C6. The peaks at 80 ppm and 102.5 ppm are assigned to C4 and C1 bearing an unsubstituted hydroxyl group, respectively. A peak present around 99 ppm marked as C1' is assigned to a C1 carbon adjacent to C2 carbon bearing a substituted hydroxyl group; and a peak around 75,7 ppm marked as C4' is assigned to C4 carbon adjacent to C3 carbons bearing a substituted hydroxyl group. The resonance peaks of C2, C3 and C5 carbons give a strong cluster around 70 – 72.5 ppm. The signals at 170, 169 and 168.7 ppm are assigned respectively to the carbonyl carbons linked to C6, C3, and to C2 [33]. The Figure 3C shows the DEPT-135 spectrum of the cellulose acetate (DS2.3), the evidence of the reaction is shown by a change in orientation of the cellulose skeleton C6 carboone by 120 ° (C6s and C6) and the disappearance of the carbonyl ester (quaternary C8).

3.1.3. X-ray diffraction (XRD)

The X-ray diffraction pattern of unmodified cellulose and cellulose acetate (DS≈2,3) samples (Figure 4) shows four peaks at 2θ = 15° ; 16.5° ; 22.7° and 34.5° and are respectively assigned to the lattice plane of Miller indices (101) (101¯) , (002) and (040) indicating , thus , the cellulose sample is a type I polymorphism [34] .

In addition, the value of the crystallinity index calculated from the diffraction patterns [35] has awakened a great starting cellulose crystallinity (I_C = 90,63%). After acetylating, the peaks characterizing the native cellulose disappear. So, the cellulose acetylating leads to a destruction of crystalline order and the formation of amorphous CA.

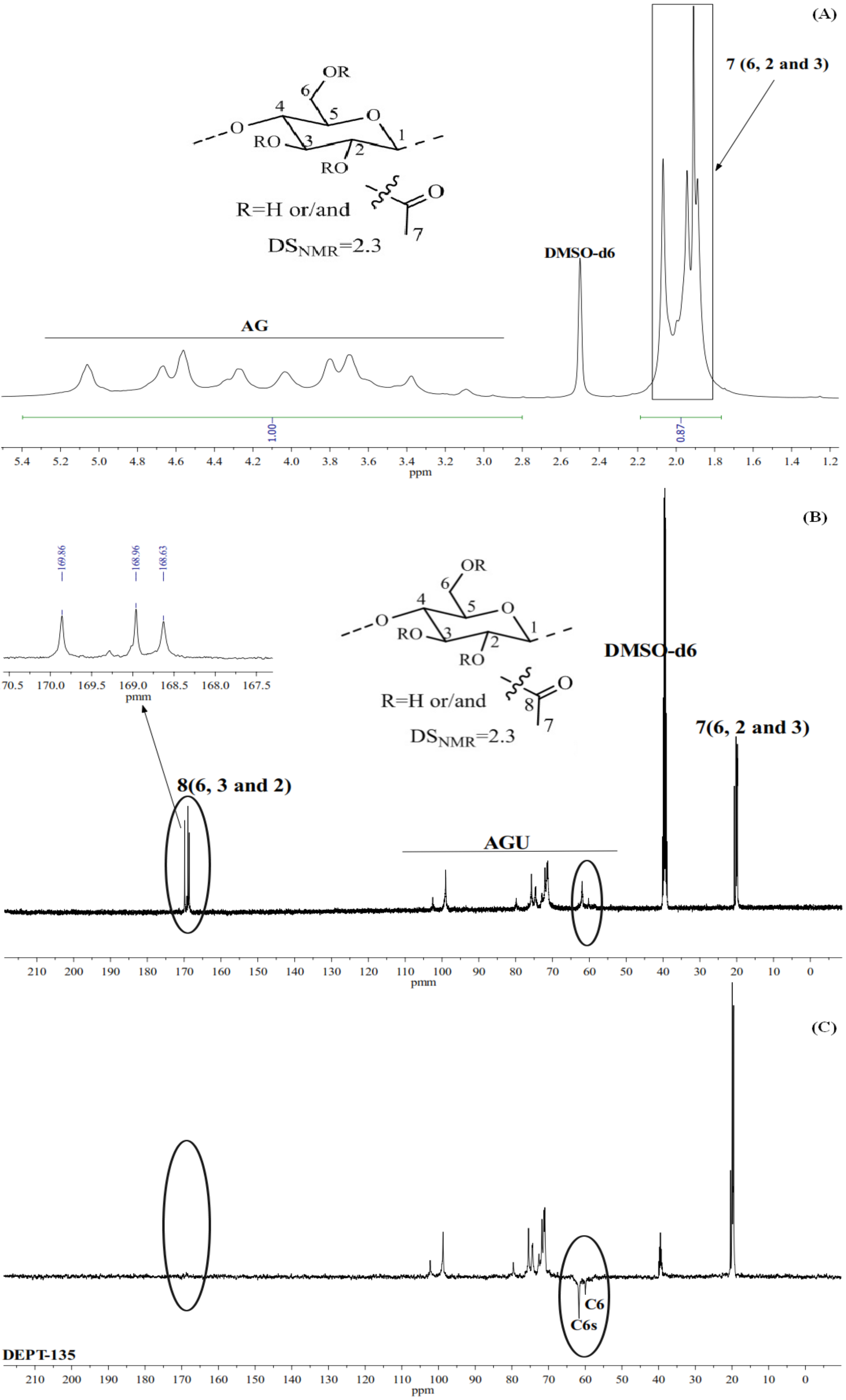

Figure 3: NMR Spectra of: (A) ^{1}H NMR, (B) ^{13}C NMR and (C) DEPT-135 spectra of cellulose acetate (DS2.3)

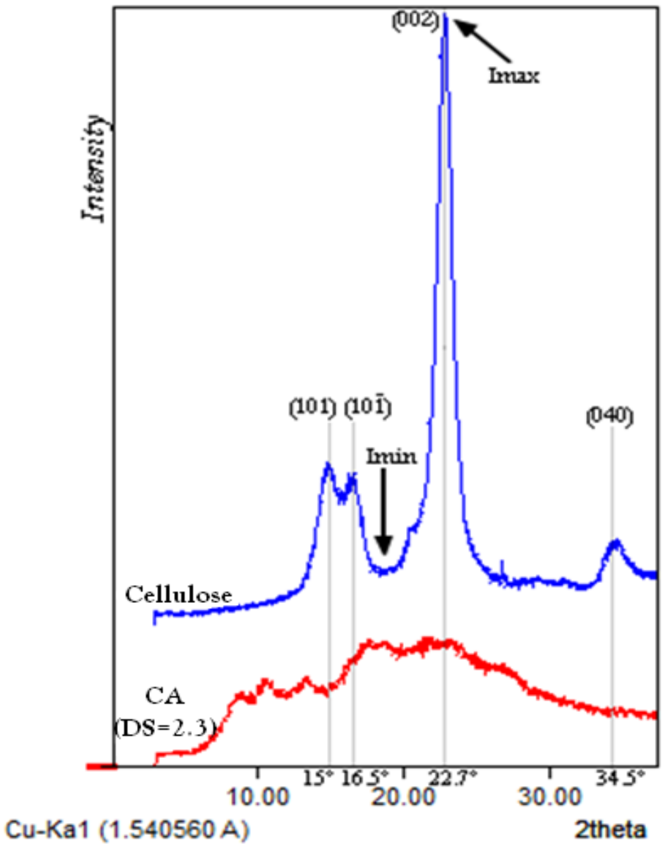

Figure 4: x-ray diffractogrammes of the unmodified cellulose and CA (DS2.3)

3.2. Determination of the surface tension γ of cellulose acetate samples depending on DS

Predicting the surface tension or rheological behavior of typical materials is a very complex and difficult task. In addition, hydrophobic-hydrophilic type interactions can cause processes of association between intra- or interchain hydrophobic units leading to self-assembled and more compact micellar structures. However, the solutions or the dispersions containing surface-active molecules (like surfactants, amphiphilic compounds, lipids, proteins etc.) are usually characterized by a reduced level of equilibrium surface tension because they adsorb on interfaces.

Surface tension (**γ**) is one of the most important parameter characterizing cellulose and its derivatives. Though, the diversity of its values reported in the literature led us to conduct this study at the end to explain this variation in the data (table 1). In the first time, we aimed to highlight the influence of the degree of substitution on the variation of surface tension of cellulose acetate samples and generally cellulose derivatives, and in the second one, to determine the relationship between the surface tension and the solubility parameters (δ_t). To carry out this task, we have prepared several CA samples with different DS and their surface tension values γ were calculated using the Parachor equation proposed by *Quayle et al.* [36]. The Parachor *P* was calculated using group contribution method by means of the following equation (eq.7):

$$P = \left(M * \gamma^{\frac{1}{4}}\right)\rho \quad and \;\; P = \sum P_i \quad (7)$$

Where, P is the Parachor coefficient $(m^3.mol^{-1})(N.m^{-1})^{\frac{1}{4}}$, M is the molar weight $(g.mol^{-1})$, γ is the surface tension (m$N.m^{-1}$)ou (m$J.m^{-2}$), ρ is the volumetric weight $(g.cm^{-3})$ and P_i is the partial parachor of group i in the chemical structure of the repetitive unite (monomer).

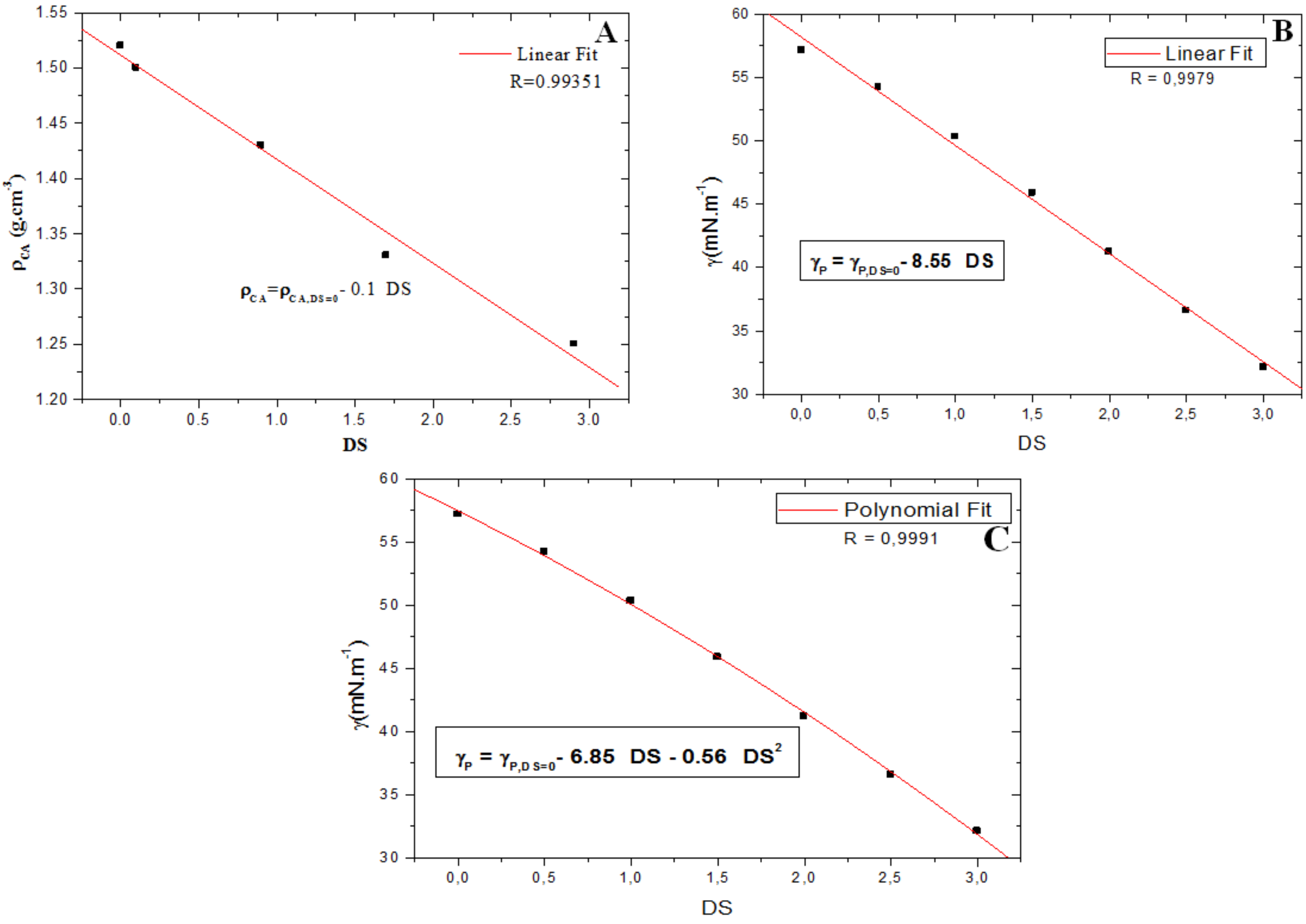

Figure 5: (A) Variation of the density (ρ $_{CA}$) of cellulose acetate samples as function of DS_{CA}, (B) Linear empirical equation between γ_{CA} and DS_{CA}, (C) Polynomial empirical curve of γ_{CA} and DS_{CA}

In the case of cellulose acetate sample the relationship between the surface tension, density and substitution degree becomes:

$$\gamma = \frac{\rho_{CA}.P}{162 + 42DS} \qquad (8)$$

First, we determined experimentally the density (ρ_{CA}) of cellulose acetate at different degree of substitution (DS) (figure 5A). The experimental results show a linear relationship between these two parameters. The Parachor values (P) of cellulose acetate samples (CA) depending on of the values of DS is calculated using the group contribution method (GCM) [36], and the values of the parameter Parachor obtained are introduced in the equation (8), which the relationships between P, γ, ρ_{CA} and DS_{CA} were deducted. The results obtained are used to plot the surface tension as a function of DS, where, we are compared the linear and the polynomial empirical relations, in all cases, we note that the surface tension γ_{CA} values decrease increasing the DS_{CA} value of cellulose acetate. This result is adequate because the cellulose acetate surface becomes more hydrophobic when DS_{CA} increases and the surface energy change also. However, the variation of the surface tension ($\gamma_{CA)}$ depending on the DS_{CA} shows a linear dependence with a correlation coefficient of 0.9979 (Figure 5B) and a polynomial variation with a correlation coefficient 0.9991 (figure 5C).Upon addition of acetyl group, the OH groups were removed and the hydrophilicity decreases to obtain hydrophobic cellulosic fibers. Therefore, the hydrophobicity due to the insertion or grafting of acetyl groups to the polymer resulted in a decrease in a decrease in the surface tension.

3.3. Relationship between surface tension, solubility parameter and DS_{CA}

The solubility parameters (δ_t) of cellulose acetate samples depending on their substitution degree (DS_{CA}) were calculated according to *El Barkany et al.* procedure [13] using the group contribution method of *Van Kerevlen* [3].

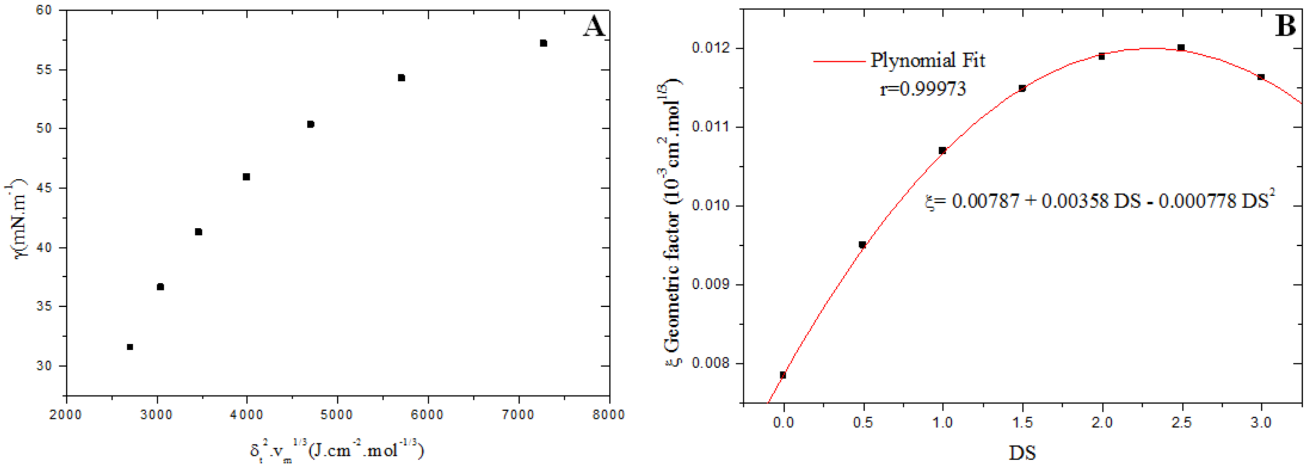

Figure 6: (A) Dependence of surface tension γ_{CA} and the solubility parameter of cellulose acetates (δ_t), **(B)** Dependence of geometric factors and DS_{CA}

Analyzing the results reported in the allure of figure 6, we noted that increasing the DS values of cellulose acetate samples from 0 to 3, the solubility parameters (δ_t) and surface tension (γ_{CA}) values decreases from 42.11 to 21.65 $j^{1/2}.cm^{-3/2}$) and 57.17 to 31.52 (mN/m) respectively. However, the empirical relationship between the surface tension and DS was extracted from the regression method in its general form (equation 9):

$$\gamma_{CA} = (\alpha + \beta\ DS + \mu\ DS^2)\ \delta_t^2 v_m^{1/3} \qquad (9)$$

From the regression curve we determined the values of α, β and γ : $\alpha = 7.87\ 10^{-6}\ cm^2 mol^{1/3}$, $\beta = 3.58\ 10^{-6}\ cm^2 mol^{1/3}$ and □= $0.778\ 10^{-6}\ cm^2 mol^{1/3}$. From this results, we can noted clearly the relation between α, β and γ, where □= 0.1α and $\beta = 0.5\alpha$. The new relationship equation (eq.10) between γ_{CA} and δ_t was:

$$\gamma_{CA} = \alpha(1 + 0.5\ DS + 0.1\ DS^2)\ \delta_t^2 v_m^{1/3} \qquad (10)$$

Conclusion

The introduction of a functional group into a hydrophilic group in cellulose fibers changes the surface activity of these materials. The functional group shows novel properties providing the possibility of expanding the utilization of cellulose. In this study, we have highlighted the hydrophobicity brought by the grafted acetyl groups onto cellulose backbone. This acetylated cellulose may be exhibit amphiphilic behavior.

Calculations of Parachors (P) and densities of cellulose acetate samples (CA) at different substitution degree (DS) make to find a binding relationship with the surface tension γ_{CA} and DS. These equations show that the surface tension variation as a function of DS can be linearly or polynomial traces, which explains that the surface tension of the cellulose acetate is highly character depends on its degree of substitution. The object of a correlated study is the determination of optimal conditions that allow these systems to be eligible as wall material for capsules. These capsules may be useful for the design of cellulose-based food ingredients with specific functional characteristics or for the encapsulation of hydrophobic molecules in cosmetic field. In this latter case, alkylated cellulose would be particularly useful.

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