New approach to predict the solubility of polymers
Application: Cellulose Acetate at various DS, prepared from Alfa "*Stipa -tenassicima*" of Eastern Morocco

A. Elidrissi [1*], S. El barkany [1, 2], H. Amhamdi [2], A. Maaroufi [3], B. Hammouti [1]

[1] *LCAE-URAC18, Faculty of Sciences,University Mohammed Premier, 60000 Oujda, Morocco.*
[2] *Physical Chemistry Laboratory of Natural Resources and Environment, National School of Applied Sciences in Al Hoceima, University Mohammed Premier, 32 003 Al Hoceima, Morocco.*
[3] *Faculty of Sciences, Chemistry department, University Mohammed V Rabat, Morocco*

Abstract

Cellulose triacetate (CA, DS~3) was prepared starting from Alfa "*Stipa-tenassicima*" cellulose, acetic anhydride in acetic acid/toluene and perchloric acid which was used as catalyst. Cellulose acetate samples having various DS were elaborated by saponification reaction in alkali medium. The synthesized product was characterized by FTIR. Substitution degree (DS) of CA was directly determined by a classical titration method, it can also be obtained using the ratio of the areas of the carbonyl ester A(C=O) peak and the hydroxyl A (O—H) peak detected on FTIR spectra. We have studied and discussed in the context of usage in modification reactions, the solubility of the CA samples by varying their DS. This investigation was based on the determination of the Flory-Huggins interaction parameters (χ_{sp}) using the partial Hansen solubility parameters (HSP). HSP of Cellulose and the CA samples were calculated from the *Van-Krevlen-Hoftyze* (VKH) method and the T. Lindvig approximation. We have focused our work on predicting and controlling family solvents of CA with various DS, in order to facilitate and to optimize the homogenous modification reaction conditions. From results on a range of CA samples, it is conclude that their prediction solubility taking the value of DS into account is possible, and then the surface modification can relatively be easily realized. We have shown that the theoretical study is in good agreement with the experimental tests.

Keywords: Alfa "Stipa -tenassicima" Cellulose; Plastic films; acetylation; substitution degree; solubility.

Introduction:

Cellulose is the natural most abundant linear polymer. Its isolation and purification represent one of the largest activities [1]. Cellulose also is the basis of a large industry [2, 3], and it will be useful to look for improvements as well as for environmental safety. Its advantages are that it is renewable, biodegradable, and biocompatible and can be derivatized to yield various useful products [4, 5]. Yet, cellulose is hardly ever used as a chemical raw material because of its poor solubility resulting mainly from the highly extended hydrogen bonding of its anhydroglucose repeat units. This phenomenon has been a stumbling block in its appropriate utilization and prevents cellulose from being processable by normal melt (or solution) technologies. This processing handicap is conventionally overcome by chemical modification of cellulose, generally accomplished heterogeneously [6].

The dissolution step usually proves to be cumbersome or expensive, or results in extensive degradation of the macromolecular backbone. Some solvents have been reported, but they are seldom useful for a wide range of synthetic reactions [7, 8]. For example N, N dimethylacetamide (DMAc) containing lithium

chloride is a solvent system used frequently in polysaccharide chemistry and causes a faster dissolution of the material [9-15]. However, the solubility gain is not only due to improved activation, swelling or breaking of hydrogen bonds, but also due to a degradation of the high molecular weight distribution of the pulps. All activation treatments accelerate the dissolution rate, cause intra and inter-crystallite swelling, break hydrogen bonds and increase accessibility [16, 17].

A number of cellulose derivatives are currently prepared under heterogeneous conditions. Cellulose esters are generally synthesized employing an anhydride with a catalyst or an acid chloride in the presence of a tertiary base [18]. However, problems arise such as poor uniformly of substitution; low yields and extensive by product formation, consequently there is much interest in developing new acetylating methods to provide products with novel characteristics [19]. For a maximum conversion of cellulose to its derivatives, it is advisable to carry out the reaction in a homogeneous medium, requiring a suitable solvent system [20-22]. The search for new systems and process is important on environmental grounds, because problems tend to be focused around optimization and ecological issues.

Chemical modification has been used as means of improving and enhancing solubility of cellulose and its derivatives by using appropriate chemical entities such as: introducing water-soluble entities, hydrophilic moieties, bulky and hydrocarbon groups, etc [6]. The cellulose ether is commonly introduced into industrial formulations in order to improve workability of the fresh material and adherence to the substance. Cellulose acetate (CA) is a polymer of great importance whose industrial uses include yarn for the textile industry, filters, photographic films, transparent and pigmented sheeting and plastic compositions such as those used for compression, extrusion, injection moulding and, to a lesser extent, surface coatings, etc. The degree of substitution *(DS)* of CA, i.e. the average number of acetyl groups per anhydroglucose unit, can range from 0 in the case of cellulose, to 3 for the triacetate cellulose. So, it is very important to study the solubility of Cellulose acetate in order to enhance its properties by grafting other each group in addition to acetyl groups. In the present work, we describe the synthesis of cellulose acetate at various DS soluble in most organic solvents such as THF, starting from *Alfa "Stipa-tenacissima"* cellulose of Eastern Morocco**.** It is known that the dissolution mechanisms of cellulose derivatives fibers are strongly dependent on the solvent quality and biopolymer structure respectively. The aim of this study was to better understand the dissolution mechanisms of CA fibers in organic solvent systems and to better identify the influence of different DS values on dissolution capacities. The Hansen Solubility Parameters (HSP) determined by indirect measurements using the *Van-Krevelen-Hoftyzer* (VKH) method and the *T. Lindvig* approximation [23], have been employed to develop a method capable of predicting and controlling dissolution of cellulose derivatives in different solvent conditions, taking into account DS values. The theoretical results are verified by experimental tests. Solubility can be improved greatly, and then the fabrication of functionalized materials can relatively be easily carried out [24].

Theoretical background

An appreciation of the meaning of the solubility parameter in physical terms can be obtained from a study of Fig. 1. Parts A and B, in a schematic fashion, the basic assumption in the solubility parameter concept is that there is a correlation between the cohesive energy density (CED) (potential energy per unit volume) and mutual solubility.

The CED is the energy of vaporization (ΔEvi) per cm^3. The solubility parameter has been defined as the square root of the CED and describes the attractive strength between molecules of the material [27].

$$\delta_i = \left(\frac{\Delta E_i^V}{V_i}\right)^{1/2} = (CED)^{1/2} \qquad (1)$$

The Hildebrand parameter defined by Eq. (1) has proved useful for regular solutions i.e., solutions without molecular polarity or specific interactions, and good estimates of excess Gibbs energy (and consequently activity coefficients, etc.) It is still used for various purposes in non-regular solutions, but to some extent has been superseded by multi-component solubility parameters [28, 29].

According to the Hansen solubility parameter theory [30], the energy of vaporization can be divided into contributions of non-polar (dispersion) forces (d), polar forces (p) and hydrogen-bonding (h_b) eq.3:

Elidrissi et al.

$$\Delta E_V = \Delta E_{coh} = \Delta E_d + \Delta E_p + \Delta E_h \qquad (2)$$

The Hildebrand solubility parameter can be expressed in terms of the three Hansen solubility parameters related to each contribution [31]:

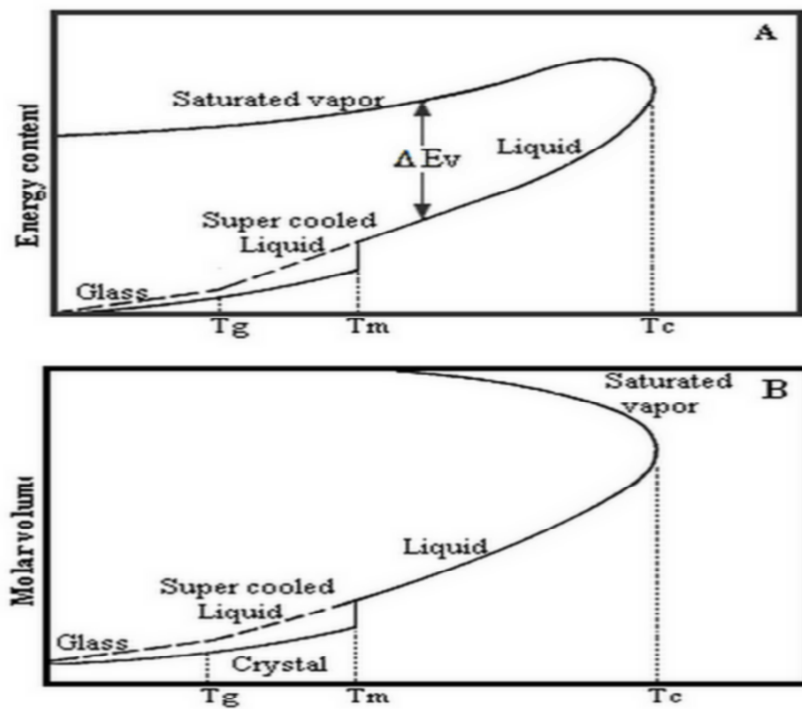$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (3)$$

Figure 1 Dependence of energy content (A) and molar volume (B) on temperature [26]

The corresponding equation for the mixing enthalpy can be calculated by

$$\Delta H_m = \emptyset_S \emptyset_P (\delta_S - \delta_P)^2 \qquad (4)$$

where ΔH_m is enthalpy of mixing per unit volume, δ_S and δ_P are solubility parameters of solvent and polymer respectively [32]. Eq. (5) predicts that $\Delta H_m = 0$ if $\delta_S = \delta_P$, so that two substances with equal solubility parameters should be mutually soluble due to the negative entropy factor, this is in accordance with the general rule that chemical and structural similarity favors solubility. As the difference between δ_S and δ_P increases, the tendency towards dissolution decreases [32].

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

By using Eq. (4) and (5) H_m becomes:

$$\Delta H_m = \emptyset_1 \emptyset_2 \left[(\delta_{dS} - \delta_{dP})^2 + (\delta_{pS} - \delta_{pP})^2 + (\delta_{hS} - \delta_{hP})^2 \right] \qquad (6)$$

A solvent, therefore, with given values of $\delta_{p,S}$, $\delta_{d,S}$ and $\delta_{h,S}$ is represented as a point in space, and δ_t is the vector from the origin to this point. Furthermore, it has been found on a purely empirical basis that if δ_{dP} is plotted on a scale twice the size as that used for δ_{pP} and δ_{hP}, then all solvents that dissolve the polymer fall

within a sphere of radius R surrounding the point ($\delta_{p,P}$, $\delta_{d,P}$ and $\delta_{h,P}$) [33]. The Hansen theory may, therefore, be considered a graphical quantification of the old ''like dissolves like'' concept of solubility (figure 2). *Skaarup and Hansen* [34, 35] have developed an equation for the solubility parameter 'distance', D_{SP}, between two materials (solvent-polymer) based on their respective partial solubility parameter components :

$$D_{SP} = \left[4(\delta_{dS} - \delta_{dP})^2 + (\delta_{pS} - \delta_{pP})^2 + (\delta_{hS} - \delta_{hP})^2 \right]^{1/2} \quad (7)$$

A region of solubility has been characterized by the distance between solvent and polymer coordinates [36, 37]. Each polymer, P, was characterized by a set of Hansen parameters defining the center of the solubility sphere and an interaction radius ^{P}R (fig.2). To predict the solubility, the distance D_{SP} between the position ($\bar{\delta}_{dS}, \bar{\delta}_{pS}, \bar{\delta}_{hS}$) and the center of the sphere of solubility ($\delta_{dP}, \delta_{pP}, \delta_{hP}$) must be less than the interaction radius ^{P}R.
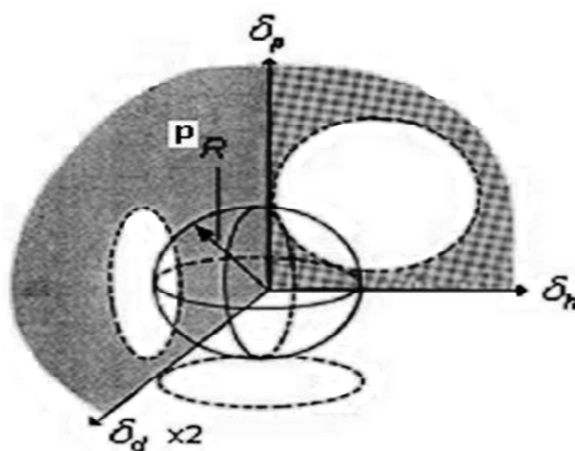

Figure 2 Representation of a Hansen parameter solubility sphere and its projections on three axial planes (adopted from *Beerbower and Dickey*, http://www.dbe.dupont.com).

If the distance between the solvent and the polymer position exceeds ^{P}R, the two components are not soluble, or swelling is less than expected.
The doubling of the δ_d scale, leading to the factor ''4'' in the first term, was intended to make the ''volume of solubility'' approximately spherical [38]. This factor is theoretically predicted by *Prigogine* [39] when the geometric mean is used to estimate the interaction in mixtures of dissimilar molecules.

Methods for determination of solubility parameters:
Hildebrand parameters cannot be calculated directly for polymers from heat of vaporization data because of their no volatility. However, it is calculated using the indirect correlation or atomic contribution group method.

Indirect methods
The determination techniques for polymer solubility parameters have been widely described in literature, solvency testing (screening procedure) [40], osmotic pressure [26], swelling values [40– 42], turbidimetric titration [43, 44], specific volume [45], intrinsic viscosity [46- 48], inverse gas chromatography [49, 50] and Matrix Assisted Laser Desorption Ionization, MALDI [51].

Correlation methods
Some of the techniques based on the correlation methods are dipole moment [52], refractive index [52, 53], H-bonding parameter [54], surface tension [55], dielectric constant [56], Flory–Huggins interaction parameter [57]. The simplest technique for the determination of polymers solubility parameters is the group contribution method, based on the   assumption of different functional groups contribution [58].

Atomic group contribution methods
The previous methods have been used to estimate the solubility parameter [26, 59–63]. VKH [64], Fedors [26] and Barton [65] have reviewed these methods and tables of group values had been given. The molar volume of solvents and polymers can also be estimated by group contribution techniques.

Van Krevelen and Hoftyzer method (VKH)
In order to determine the total polymers solubility parameters, using these calculations, VKH used the molar volumes and molar attraction constants of the repeating unit so as to calculate the partial solubility parameter of the polymer. The solubility parameter components may be predicted from group contributions, using the following equations (VKH) [32, 66 – 68].

$$\delta_d = \frac{\sum F_{di}}{\sum V_i} \qquad (8)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{\sum V_i} \qquad (9)$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{\sum V_i}} \qquad (10)$$

The dispersive Hansen parameter treats the molar attraction constants as additive. The polar Hansen parameters also are additive, unless more than one polar group is present. The molar attraction constant is not applied to the H-bonding Hansen parameter. Rather, an H-bonding energy, E_{hi}, is used [36].

Calculation of the Flory parameter:
According to the regular solution theory, the relationship between the Flory–Huggins interaction parameter and the solubility parameters is [69]:

$$\chi_{SP} = \frac{V_S}{RT}(\delta_S - \delta_P)^2 \qquad (11)$$

Peppas et al. [70] have calculated Flory interaction parameters on the basis of the following procedure [47] using the corresponding solubility parameters of two components. In general, the interaction parameters, χ is defined as:

$$\chi_{SP} = \frac{zX_S \Delta w_{SP}}{kT} = \chi_H + \chi_S \qquad (12)$$

where z is the lattice coordination number, X is the number of polymer segments relative to solvent, Δw is the interaction energy. The term χ_S is the entropic contribution of approximately 0.34. The term χ_H is the enthalpy contribution and can be calculated from solubility parameters as shown by *Mikos et al.* [71]:

$$\chi_H = \frac{V_S}{RT}[(\delta_S - \delta_P)^2 + 2I_{SP}\delta_S\delta_P] \qquad (13)$$

In which I_{12} is a binary interaction parameter. For the system consisting of two components with a similar chemical structure, $I_{12} = 0$. The following equation is obtained:

$$\chi_{SP} = 0.34 + \frac{V_S}{RT}(\delta_S - \delta_P)^2 \qquad (14)$$

For the estimation of Flory–Huggins interaction parameters Hansen [72] has used the following equation with $\alpha = 1$:

$$\chi_{SP} = \alpha\frac{V_S}{RT}\left[(\delta_{dS} - \delta_{dP})^2 + 0.25(\delta_{pS} - \delta_{pP})^2 + 0.25(\delta_{hS} - \delta_{hP})^2\right] \qquad (15)$$

Lindvig et al. [23] have estimated Flory–Huggins interaction parameters from the Hansen parameters with an optimum value of the correction constant $\alpha = 0.6$ [23]. As mentioned, the correction constant was different for different species pairs. According to the Flory-Huggins model a polymer and solvent are

Elidrissi et al.

completely miscible if $\chi_{SP} < 0.5$ $(1+ (V_{mS}/V_{mP})^{1/2})^2$. In this work the relationships used for calculate the Flory–Huggins interaction parameter is the Lindvig correction, because it was optimized according to the structure of polymer synthesized; CA (polar, H-bonding…).

Experimental and methods

Materials

Alfa *"Stipa-tenacissima"* cellulose fibers were dried in a vacuum oven at 90 °C for 48 h before use for modifications. Toluene, Tetra-HydroFurane (THF) and glacial acetic acid, products of Aldrich were dried before their used. *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.

Isolation of cellulose from Alfa "Stipa-tenacissima"

Native *Alfa "Stipa-tenacissima"* fibers used in this work were purchased in Oriental (eastern) Morocco. Cellulose was extracted according to the *El Idrissi et al.* method [25]. Alfa fibers were cut until fine particulate fibers were obtained. Then, the fibers were treated with a 1N NaOH solution at 80 °C for 2 h under mechanical stirring. This treatment was done three times, in order to purify cellulose by removing other constituents present in the fibers. After each treatment, fibers were filtered and washed with bleach (NaClO) and distilled water until the alkali was completely eliminated and washed again with ethanol and ether diethyl three times.

Preparation of Cellulose acetate at varying DS

The starting cellulose acetate DS~2.9 was prepared from Alfa *"Stipa-tenacissima"* cellulose in toluene/acetic acid mixture using a catalytic amount of Perchloric acid. 1 g of Alfa *"Stipa-tenacissima"* cellulose 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 reaction was kept at room temperature and the solution was kept under stirring for 15 min. the Claire solution obtained was precipitated in distilled water, the product was recuperated by filtration under vacuum and washed by distillated water frequently, and dried at constant weight at 40 °C and stayed one week in dissicator with P_2O_5.

The cellulose acetate samples were prepared by the 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. More ever, 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^{-3} 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 dissicator, until constant weight. Liberated acetic acid (DS) quantities were determined by the classical volumetric titration using phenolphthalein as indicator and compared with those obtained using FT-IR data.

DS Determination (Volumetric method):

Firstly, we de-acetylated Cellulose acetate partially in order to obtain the desired DS. Then, a second de-acetylation was realized totally in order to determine the DS of each sample recovered after the partial de-acetylation. The de-acetylation reaction was kept at room temperature for 24 h under stirring, and the resulted solution was titrated by 0.15 M acetic acid solution using phenolphthalein as indicator coloring. The normality of the white solution (basic solution without CA) was titrated and it was around $N_{KOH} = 0.18$ M. For 10 ml of de-acetylation solution, the results were summarized in Table I.

Table I Preparation conditions of CA at various DS_{AC}. (P): Partial deacetylation and (T): total deacetylation

Sampl.	Weight of KOH (g) in 100 ml of ethanol [P]	Weight (g) of KOH in 100 ml of ethanol [T]	$V_{CH3COOH}$ ml	DS_{AC}
white solution	0.0	1	12	0.0
1	0.0	1	5.2	2.9
2	0.2	1	7.1	1.7
3	0.4	1	9.0	0.9
4	0.6	1	11.6	0.1

The DS_{AC} value was calculated using the equation16:

$$DS_{AC} = \frac{(M_{AGU} \cdot \Delta n_{KOH})}{(m_{sample} - \Delta n_{KOH} \cdot M_{ac\,l})} \quad (16)$$

In which:

DS_{AC} = degree of substitution of acetyl group

M_{AGU} = AGU monomer molar weight = 162 g.mol^{-1}

Δn_{KOH} = molar number variation of KOH before and after saponification

$M_{ac\,l}$ = acetic liberated group molar weight = 42.04 g mol^{-1}

Spectroscopic measurements

The chemical structures of samples were evaluated by FTIR. FTIR spectra were obtained on a Shimadzu Fourier transform infrared spectrometer FTIR- 8400S using a KBr disc containing 2% finely samples. Twenty scans were taken of each sample recorded from 4000 to 400 cm-1.

Casting

The plastic films of cellulose acetate were obtained by the casting method, 1 g of the CA samples were dissolved in 30 ml of solvent according to the solubility diagram. Each solvent was eliminated by evaporation process under vacuum.

Solubility study

The experimental results for the description of the solubility have been obtained by test solvents, where; the spatula point of the CA samples was added to ~3 ml of each solvent. CA samples have been used in the granular form (as prepared).

Results and discussion

FT-IR analyses

Figure 4 shows the spectra of the CA samples and Alfa *"Stipa-tenacissima"* cellulose. Two peaks were of great interest: the carbonyl peak at 1749cm^{-1} and the hydroxyl peak at 3420 cm^{-1}. The area of the carbonyl peak was then recorded as well as the area peak of the hydroxyl group (OH) in absorbance mode (*Table II*). For the CA samples, the *DS* was already determined by the volumetric method, a graph of the ratio of the areas of the OH peak for the carbonyl peak *versus DS* could be plotted and the curve obtained is in agrement with the results published by *E. Samios et al.* **[73].** The DS values of the CA samples can be calculated using the absorption band areas of the functions existing in their structure (C= O and O–H), obtained by FTIR spectra of any CA sample (figure 3). FTIR spectroscopy is a very powerful tool in the characterization of CA as it provides an alternative method for calculating the *DS*.

Table II shows the relationship between the *DS* and the ratio of the hydroxyl peak area to the carbonyl peak area. From the data, the graph of the ratio of the peaks versus the *DS* was plotted. From this calibration curve the *DS* of any CA sample can be calculated once the *FTIR* spectrum is available.

Table II The ratios values of OH over CO peak areas A_{OH}/A_{CO} for CA *as* calculated from the volumetric method

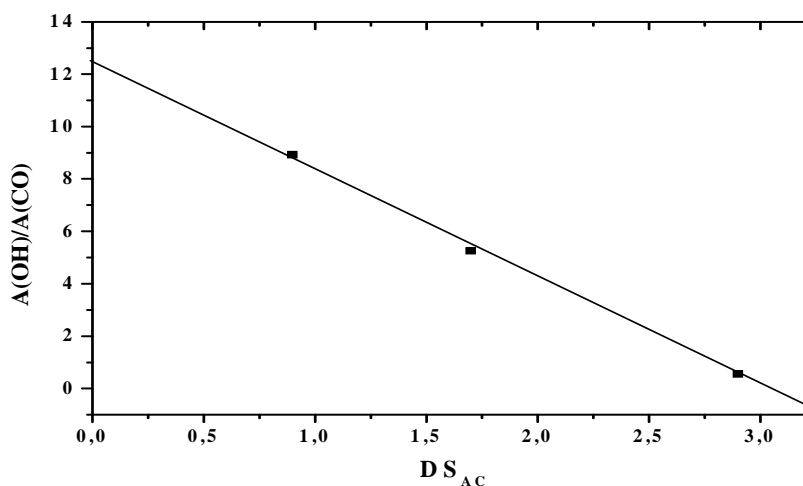| DS_{AC}	A_{OH}	A_{CO}	A_{OH} / A_{CO}
2.9	26.371	47.912	0.55
1.7	97.517	18.575	5.25
0.9	192.466	21.574	8.92

Figure 3: Graph of A_{OH} / A_{CO} versus DS_{AC}

FTIR spectra of the Alfa *"Stipa-tenassicima"* cellulose and the acetylated cellulose at various DS; CA (2.9), CA (1.7), CA (0.9), CA (0.1) are shown in figure 4. It can be seen that the all spectra of cellulose acetate samples show similar spectral features and no new absorption bands result after de-acetylation, indicating no chemical reaction occurred during the cellulose de-acetylation process. The cellulose acetate spectra provide an evidence of acetylation by showing the reduction of OH frequency and the appearance of the three new important and characteristic absorption bands of ester acetyl group; a strong intensity band at 1749 cm^{-1} which is assigned to the stretching of the carbonyl group of cellulose acetate (C=O ester), 1373 cm^{-1} (C–H bond in an –C–CH3 group), and 1232 cm^{-1} (–C–O stretching of acetyl group) **[74, 75]**. The band located also at 1647 cm^{-1} corresponds to the bending mode of the naturally absorbed water **[76]**. In addition, the reduction in the peak intensity originates from OH stretching at 3420 cm^{-1} in CA spectra compared to Alfa *"Stipa-tenacissima"* cellulose spectrum, also indicated a partial acetylation. The total disappearance of the hydroxyl absorption band is not seen even for the sample with DS 2.9, perhaps due to adhering moisture. The absence of band at 1760–1840 cm^{-1} and 1700 cm^{-1} confirms the absence of acetic acid and acetic anhydride.

The absorption band around 1047 cm^{-1} is attributed to C–O stretching of the glucopyranose ring **[77]** and the unchanged intensity of the peak at 902 cm^{-1} assigned to β-glucosidic linkages between the sugar units suggest the non degradation of the cellulose macromolecules cross the modification reaction **[78].** The non degradability of cellulose chains my due to the small concentration of acid and alkaline solution used in the protocols, this suggestion can be affirmed by studying the macromolecular weight variation during the reaction steeps.

CA Solubility study
One of the main difficulties to the use of cellulose and cellulose derivatives in many applications is its poor solubility in organic solvents. Thus, to overcome this drawback, we have modified the Alfa "Stipa-tenassicima" Cellulose for the sake of synthesizing the CA with different DS. Furthermore, we have studied the influence of DS values on the properties of CA samples in particular on its solubility. A survey of the published data on the solubility of natural polymers in various solvents shows that dissolving power depends on the polymer and solvent structures respectively.
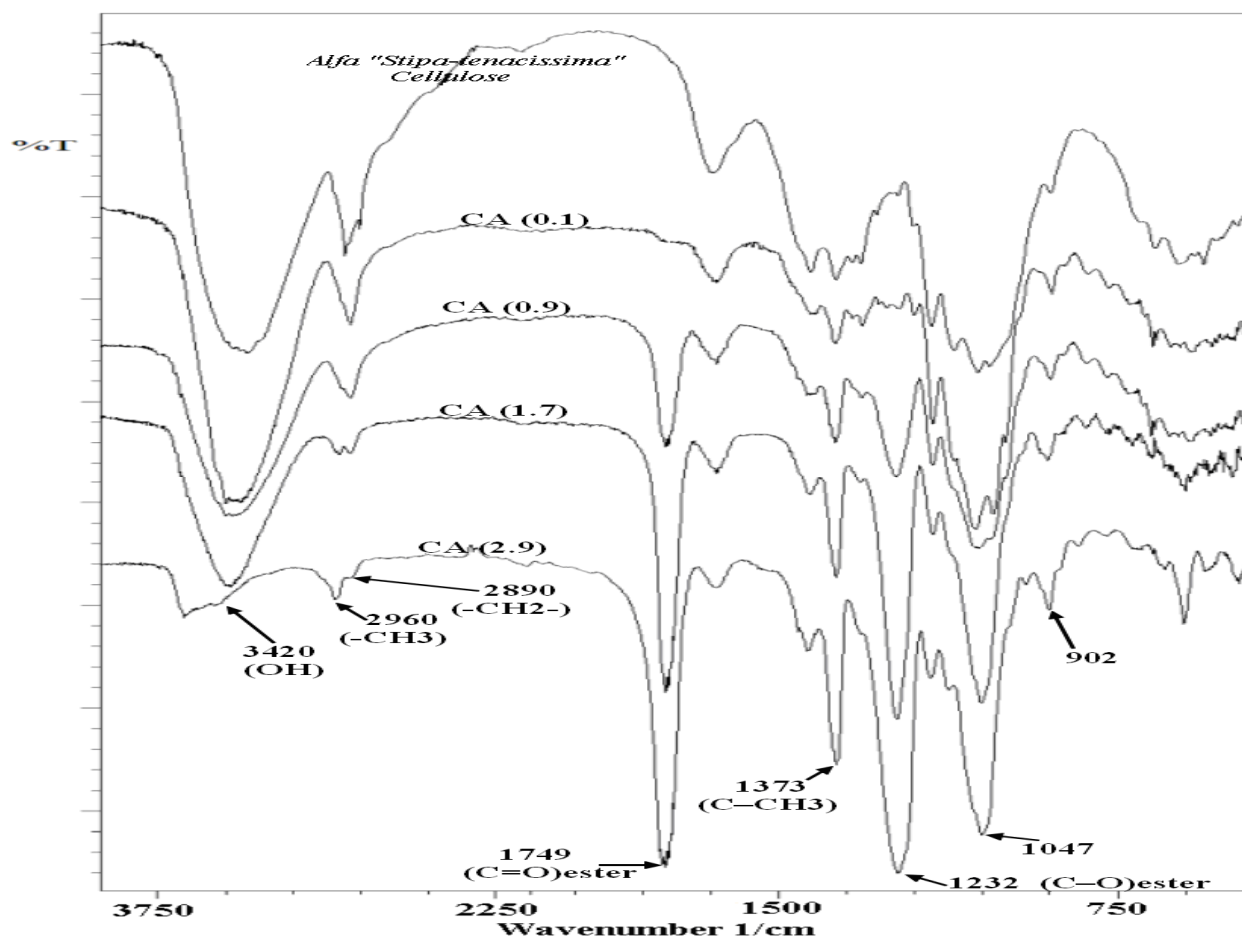
Figure 4 FTIR spectra of cellulose acetate with various DS

Table III. F_d: the dispersion component of giving δ_d, Fp: polar component, E_h: the contribution of the hydrogen bond forces to the cohesive energy of group i, and the number of group i presented in the HECA chemical formula.

Group i	Fd $J^{1/2}cm^3$ $^{/2}mol^{-1}$	Fp^2 $J\,cm^3$ mol^{-1}	E_h $J\,mol^{-1}$	Molar volumes $(cm^3\,mol^{-1})$	Number of group i presented Repeat unit						
					DS=0	DS=0.5	DS=1	DS=1.5	DS=2	DS=2.5	DS=3
-COO-	390	24010	5500	18	0	0,5	1	1,5	2	2,5	3
-CH3	420	0	0	33.5	0	0,5	1	1,5	2	2,5	3
- CH$_2$ -	270	0	0	16.1	1	1	1	1	1	1	1
> CH -	80	0	0	-0.1	5	5	5	5	5	5	5
- OH	210	25000	20000	10	3	2,5	2	1,5	1	0,5	0
- O -	100	16000	3000	3.8	2	2	2	2	2	2	2
Ring	190	0	0	16	1	1	1	1	1	1	1

Table III presents the dispersion component of giving δd (Fd), polar component (Fp), the contribution of the hydrogen bond forces (Eh) to the cohesive energy of the group i and the number of group i presented in the HECA chemical formula. The Fd, Eh and Fp (table III) were calculated using the GCM theory. The group contribution method (GCM) has proved, that the solubility characteristics of CA compounds depend greatly on the substitution degree (DS). This approach may be extended to various cellulose derivatives with various DS and grafted groups nature. From the application of the VKH method using successively the equations (8), (9) and (10) and the table III, the partial solubility parameters or the Hansen solubility parameters (HSP) were calculated and regrouped in table IV. Using these results, we have represented on figure 5 the Hansen solubility parameters [δ_t, δ_d, δ_p, δ_h, where $\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$] variation of CA at different DS.

Figure 5, shows that the variations of the total ($\delta_t = 42.11 - 21.65$ MP$^{1/2}$) and the hydrogen bond solubility parameters ($\delta_h = 20.88 - 10.78$ MP$^{1/2}$) respectively for DS situated between the values 0 and 3 are similar and decrease with increasing DS values. However, the polar ($\delta_p = 14.95 - 5.27$ MP$^{1/2}$) and the dispersion ($\delta_d = 24.42 - 18.02$ MP$^{1/2}$) components for DS situated in the range (0 – 3) have a slight variation with DS. From these results, we can conclude that the variation of the total solubility parameter (δ_t) is imposed by the hydrogen bond component. According to the fundamental of the solubility theory "like dissolve like", we can predict, easily the best solvent of any polymer.

Table IV Hansen solubility parameters of HECA at DS = 0 – 3

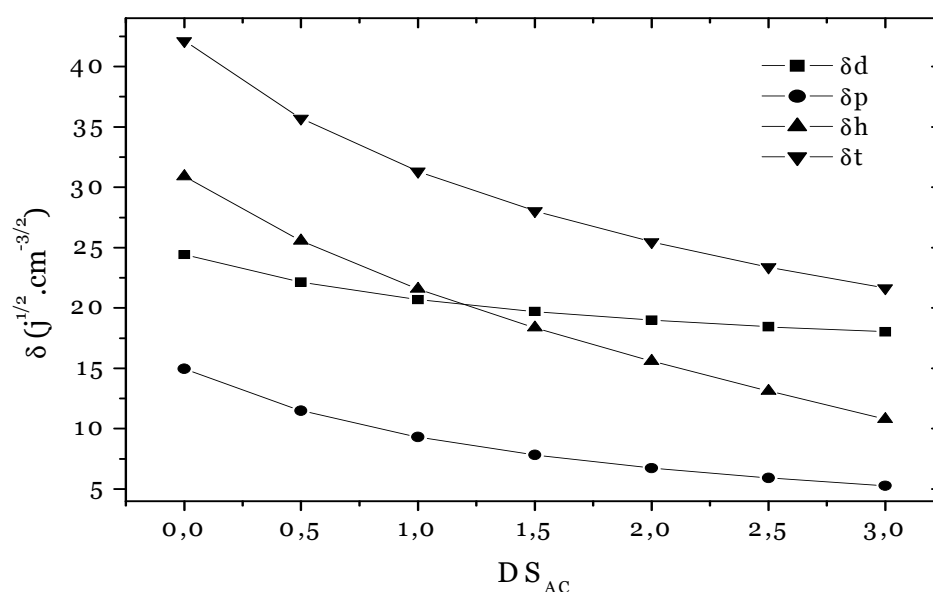| DS	δ_d (j$^{1/2}$.cm$^{-3/2}$)	δ_p (j$^{1/2}$.cm$^{-3/2}$)	δ_h (j$^{1/2}$.cm$^{-3/2}$)	δ_t (j$^{1/2}$.cm$^{-3/2}$)
0	24,42	14,95	30,88	42,11
0.5	22,12	11,47	25,56	35,7
1	20,69	9,3	21,57	31,3
1.5	19,70	7,81	18,35	28,03
2	18,99	6,73	15,59	25,48
2.5	18,44	5,91	13,12	23,39
3	18,02	5,27	10,78	21,65

Figure 5: The variation of the Hansen solubility parameters of CA at different DS.

As can be seen on the figure 5, δ_t decreases when DS of CA increases. Moreover, the solubility at low DS starts in the protic solvents and leads to the aprotic for the high DS; this may be due to the diminution of the hydroxyl group density in the material.

The combination of the partial solubility parameters (δ_h, δ_p, δ_d) variations in one graph gives important informations to choose the appropriate solvent. The useful combinations cited in literature were; the *Henry* combination (δ_h - δ_p) [79], the *Bagley et al.* combination (δ_h - δ_v), [$\delta_v = (\delta^2_p + \delta^2_d)^{1/2}$] [80], *Hoernschemeyer* combination ($\delta_h - \delta_t$) et ($\delta_a - \delta_t$) [$\delta_a = (\delta^2_p + \delta^2_h)^{1/2}$] [81]. The partial solubility parameters of some solvents were reported in the literature [37]. Using the equations 7 and 15, we can calculate the distance D_{SP} and the Flory-Huggins interaction parameter χ_{SP} between the solvent (S) and CA (P).The results are summarized in table 5, where the molar volume is equal to $V_M = M/d$, (M is the molar weight and d is the density of the solvent respectively),

Figure 6, presents the variation of D_{SP} between some solvent systems and CA polymer with different DS. The D_{SP} decreases for all solvents except the DMSO; it shows a constant D_{SP} between (DS~2.0 and DS~3), where, in this stage (DS ~ [2.0; 3.0]) the solubility was not influenced by the variation of DS. The same variations than D_{SP} were observed for the Flory-Huggins interaction parameter χ_{SP}.
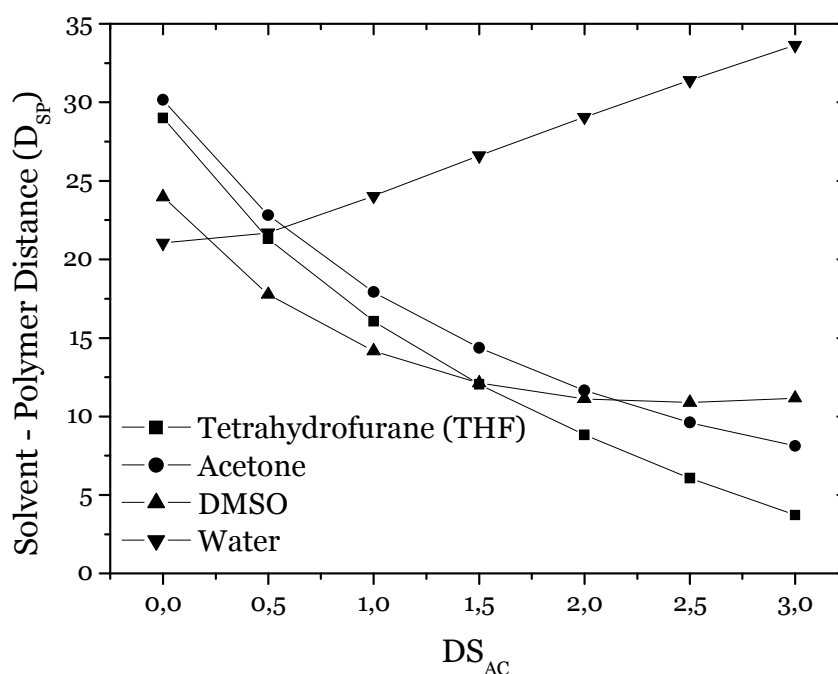

Figure 6: D_{SP} of solvents at various DS of CA.

According to the Flory-Huggins model, both polymer and solvent are completely miscible if $\chi_{SP} < 0.5$ (1+ $(V_{mS}/V_{mP})^{1/2})^2$ where V_{m1} and V_{m2} are respectively the molar volume of the solvent and polymer. It's known that the molar volume is equal to $V_M = M/d$. however, the molecular weight of polymers is very important, so, V_M be come higher than that of the solvent witch decrease the solubility of polymer in each solvent. Also, that may be the good explication to understand the relation ship between the degree of polymerization (DP) and solubility of polymers. In the present work we suppose that $V_{mP} >>> V_{mS}$, consequently the good miscibility of CA and the solvent will be reached at $\chi_{sp} \leq 0.5$.

A good correlation is noted between the theoretical (fig.7) and the experimental solubility studies (tab.VI). The factors determining the solubility of CA were studied at different levels; at the supramolecular level the solubility of CA in solvents depends on the total solubility parameter (δ_t), in particular the hydrogen bond solubility parameters (δ_h) (Figure 5). The introduction of acetate group makes the macromolecules

hydrophobic (molecular level) and insoluble in water, more than DS increases the Flory-Huggins interaction parameter (χ_{sp}) increases and the solubility of the polymer in water decreases, which explain the precipitation of cellulose acetate in water. The experimental tests are in agreement with the predictions and anticipations of theoretical study.

TABLE V
Flory-Huggins interaction parameter (χ_{sp}) and the distance (D_{sp}) between the solvent (S) and CA polymer (P) at various DS.

| solvent	V_m	CA DS=0		CA DS=0.5		CA DS=1		CA DS=1.5		CA DS=2		CA DS=2.5		CA DS=3	
		χ_{sp}	D_{sp}	χ_{sp}	D_{sp}	χ_{sp}	D_{sp}	χ_{sp}	D_{sp}	χ_{sp}	D_{sp}	χ_{sp}	D_{sp}	χ_{sp}	D_{sp}
Toluene	106.285	7,61	34,39	4,66	26,91	3,05	21,78	2,06	17,89	1,4	14,73	0,93	12,03	0,6	9,6
chloroform	80.162	4,61	30,82	2,61	23,22	1,57	17,99	0,95	14,02	0,57	10,80	0,31	8,03	0,15	5,54
1,1 Dichloromethane	78.977	5,83	34,92	3,66	27,67	2,47	22,72	1,72	18,99	1,22	15,99	0,86	13,44	0,59	11,15
Carbon Tetrachloride	96.500	7,68	36,27	4,84	28,79	3,27	23,65	2,28	19,76	1,61	16,60	1,13	13,90	0,77	11,47
Tetrahydrofuran	81.091	4,13	29,01	2,23	21,33	1,26	16,05	0,71	12,05	0,38	8,82	0,18	6,08	0,07	3,72
1,4 Dioxane	85.299	4,34	29,02	2,38	21,5	1,38	16,38	0,81	12,57	0,47	9,56	0,26	7,13	0,14	5,22
Ether diethyl	103.900	7,57	34,7	4,55	26,91	2,93	21,57	1,94	17,55	1,29	14,33	0,85	11,64	0,55	9,34
Acetone	73.518	4,05	30,16	2,32	22,82	1,43	17,92	0,92	14,36	0,60	11,66	0,41	9,60	0,29	8,12
Methyl ethyl ketone	89.573	5,33	31,37	3,11	23,97	1,95	18,95	1,26	15,22	0,82	12,28	0,53	9,88	0,34	7,90
Cyclohexanon	103.31	5,72	30,25	3,25	22,80	1,96	17,71	1,20	13,87	0,72	10,77	0,41	8,13	0,21	5,79
Ethyl acetate	98.222	5,65	30,84	3,18	23,13	1,89	18,61	1,14	13,84	0,67	10,64	0,38	7,96	0,19	5,7
Pyridine	80.558	3,8	27,92	2,11	20,8	1,25	16,04	0,77	12,56	0,48	9,91	0,30	7,85	0,2	6,34
Aniline	91.149	3,5	25,18	1,72	17,67	0,87	12,57	0,43	8,8	0,19	5,88	0,08	3,74	0,05	2,88
N-Methyl-2-pyrrolidone	96.431	4,28	11,12	2,37	7,14	1,43	4,65	0,91	12,49	0,61	10,26	0,45	8,75	0,36	7,89
N, N-Dimethylformamid	77.430	2,73	24,13	1,39	17,25	0,79	12,96	0,49	10,27	0,36	8,78	0,32	8,27	0,34	8,54
Dimethylsulfoxid	70.774	2,46	23,98	1,35	17,76	0,86	14,16	0,63	12,12	0,53	11,13	0,51	10,89	0,53	11,17
Methanol	40.221	1,04	20,69	0,51	14,44	0,33	11,59	0,29	10,98	0,33	9,58	0,41	13,03	0,53	21,93
Ethanol	58.388	1,65	21,61	0,72	21,61	0,35	21,61	0,22	21,61	0,21	21,61	0,27	21,61	0,38	21,61
Cyclohexanol	104.115	3,89	24,84	1,82	17	0,85	11,63	0,37	7,65	0,13	4,63	0,05	2,79	0,06	3,21
Water	18.054	0,48	21,04	0,51	21,70	0,63	24,04	0,77	26,61	0,92	29,07	1,08	31,4	1,24	33,65
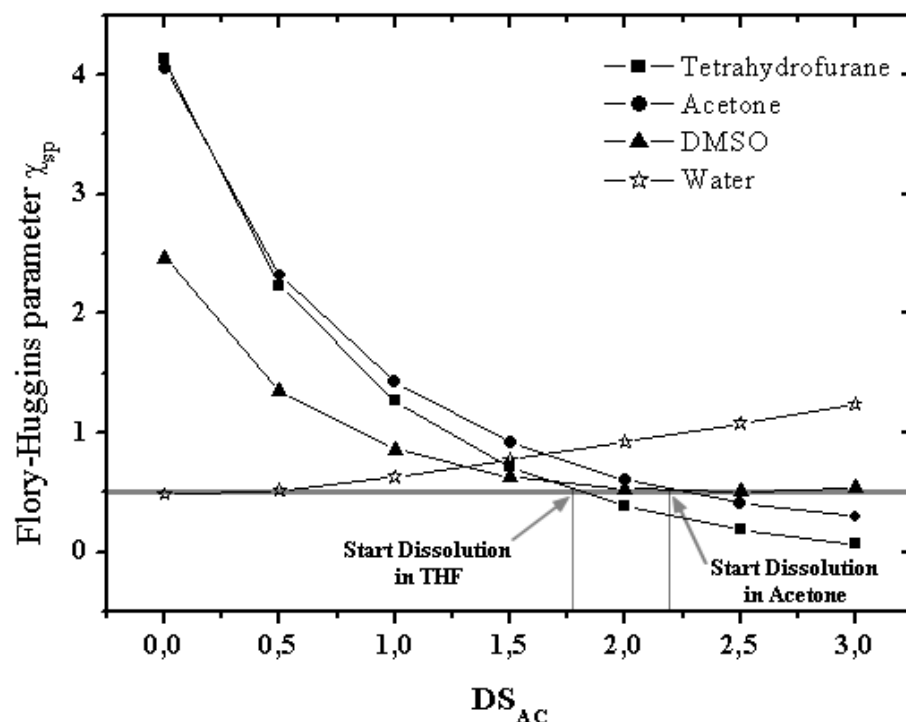
Figure 7: the variation of the Flory-Huggins interaction parameter vs. DS_{AC}.

Table VI Experimental results of cellulose acetate solubility (X= insol. ; O= sol.)

DS_{CA}	Solvent			
	Acetone	THF	DMSO	H_2O
0.1	x	x	x	x
0.9	x	x	O	O
1.7	x	O	O	x
2.9	O	O	O	x

The results obtained in this study are in good agreement with the literature data as published by *T. Heinze et al.* **[82]**. The cellulose acetate starts to dissolve in acetone from a degree of substitution around 2.2 to 2.7, depending on the molecular weight of the polymer. The solubility of the cellulose acetate with DS~0.9 in water was observed. For the cellulose acetate with DS~0 (cellulose), the theoretical results indicate that the cellulose is soluble in water, so, the non solubility noted on the experimental test may be due to the kinetic effect. Thus results indicate the possibility to modify the cellulose acetate at the DS up then 1.7 homogeneously in THF.

Conclusion
Resuming the carried out investigation we can conclude the following:
- Cellulose acetate (CA) Samples with various DS were prepared starting from cellulose extracted in alkalin medium using Alfa "Stipa-tenacissima" of Eastern Morocco. The resulted compounds were characterized by spectroscopy techniques. The DS values of acetylating were obtained from direct titration method, they can be determined by spectroscopy techniques especially FTIR. No degradation has been occurred during the process of deacetylation of CA in the alkali medium.

- The Flory-Huggins interaction parameters of CA (χ_{sp}) have been determined using the partial Hansen solubility parameters (HSP). The HSP of different samples were calculated from the *Van-Krevlen-Hoftyze* (VKH) method and the T. Lindvig approximation. At the supramolecular level the solubility of CA samples in solvents depends on the total solubility parameter (δ_t), in particular the hydrogen bond solubility parameters (δ_h). We have identified in general, the influence of DS values on dissolution capacities in organic solvent systems. It was found that with increasing DS, the solubility phenomenon increases. The dissolving power depends on the polymer and solvent structures respectively. Furthermore, the HSP can be employed to develop a method capable of predicting and controlling dissolution of cellulose derivatives in different solvent conditions taking into account their DP values. The theoretical study   that we conducted and the experimental test are in good agreement. From these results the control of solubility is possible, and the fabrication of functionalized material can relatively be easily carried out in homogenous medium.

Acknowledgment

References

1. Pondy, A.; Coccal, CR.; Nigam, P. *Bioressor Technol* 74 (2000) 69.
2. Richardson, S.; Grton, L. *Anal. Chim. Acta.* 497 (2003) 27.
3. Focher, B.; Palma, ML.; Conetti, M. *Ind. Crop. Prod.* 13 (2001) 193.
4. Mohanty, AK.; Misra, M.; Hinrichsen, G. *Macromol. Mater. Eng.* 276 (2000) 1.
5. Mohanty, AK.; Misra, M.; Drzol, LT. *J. Polym. Environ.* 10 (2002) 19.
6. Gamini, S.; Wolfgong, G. G. *Carbohydrate Polymers* 22 (1993) 979.
7. Buchanan, C.M.; Hyah, J.A.; Lowman, D.W. *Macromolecules* 20 (1987) 2750.
8. Stamin, A. J. Wood and cellulose Science, Ronald Press, New York (1964).
9. McCromick, C. L.; Callais, P.A. *polymer* 28 (1987) 2317.
10. Phillip, H.; Schleicher, H.; Wagerknecht, X. *Chem. Tech.* 7 (1977) 702.
11. Turbak, A. F.; Hammer, R.B.; Davies, R.E.; Hergert, H.L. *Chem. Tech.* 10 (1980) 51.
12. Hudson, S.M.; Cuculo, J.A. J. *Macromol. Sci.* 18 (1980) 1.
13. Tatiana, B.; Arnis, T. *Carbohydrate Polymers* 48 (2002) 23.
14. Heinze, T. *Prog. Polym. Sci.* 26 (2001) 1689.
15. Rohn, K.; Diamantaglon, M.; Kleum, D.; Berghmous, H.; Heinze, T. *Angew. Makromol. Chem.* 238 (1996) 143.
16. Liu, C.F.; Sun, R.C.; Zhang, A.P.; Ren, J.L.; Geng, Z.C. *Polym. Deg. Stab.* 91 (2006) 3040.
17. Potthost, A.; Posenau, T.; Sartori, J.; Sixta, H.; Kosma, P. *Polymer* 44 (2003) 7.
18. Shimizu, Y.; Nakayama, A.; Hayashi, J. *Cellulose Chem. Technol.* 25 (1991) 275.
19. Shimizu, Y.; Nakayama, A.; Hayashi, J. *Transaction.* 49 (1993) 352.
20. El Kafrawy, A. J. Appl. Polym. Sci. 27 (1982) 2435.
21. Morgenstern, B.; Kemmer, H. W. *Trends Polymer Sci.* 4 (1996) 87.
22. Striegel, A.M. Carbohydr. *Polymers* 34 (1997) 267.
23. Lindvig, T.; Michelsen, M. L.; Kontogeorgis, G. M. *J. Fluid Phase Equilibria* 203 (2002) 247.
24. El Idrissi, A.; El Barkany, S.; Amhamdi, H. A. K. Maaroufi. *J. App. Polym. Sci.* DOI 10.1002/app.34028
25. Ouslimane, S.; *Phys. Chem. News* 46 (2009) 135.
26. Fedors, R. F. *Polym. Eng. & Sci.* 14 (1974) 147.
27. Mieczkowski, *R. Eur. Polym.* J. 27 (1990) 377.
28. Barton, AFM. *Chem. Rev.* 75 (1975) 731.
29. Brandrup, J.; Immergut, EH. Polymer Handbook. 3rd ed. John Wiley & Sons; (1989).
30. Hansen, CM. *J. Paint Technol.* 39 (1967) 104.

31. Breitkreutz, J. *J. Pharmaceut. Res.* 15 (1998) 1370.
32. van Krevelen, DW. Properties of Polymers. Amsterdam: Elsevier Science; (1997)
33. Good, RJ. In: Patrick RL, editor. Treatise on Adhesion and Adhesives. New York: Marcel Dekker; (1967).
34. Hansen, C.; Skaarup, K. *J. Paint Technol.* 39 (1967) 511.
35. Hansen, C. Hansen Solubility Parameters—a User's Handbook, CRC Press, Boca Raton, (1999)
36. Brandrup, J.; Immergut, EH.; Grulke, EA.; Abe, A.; Bloch, DR. Polymer Handbook. 4th ed. John Wiley & Sons; (2003).
37. Beerbower, A.; Dickey, JR. Am Soc Lubric Eng Trans 12 (1969) 1.
38. Barton, AFM. CRC Handbook of solubility parameters and other Cohesion parameters. CRC Press; (1991).
39. Prigogine, I. The molecular theory of solutions. Amsterdam: North-Holland; with collaboration of Bellemans A, Mathot A., (1957).
40. Gee, G. Trans Inst Rubber Ind 18 (1943) 66.
41. Huglin, MB.; Pass, DJ. *J. Appl. Polym. Sci.* 12 (1968) 473.
42. Hamurcu, EE.; Baysal, BM. *J. Polym. Sci.* 32 (1994) 591.
43. Suh, KW.; Clarke, DH. J. *Polym. Sci.* 5 (1967) 1671.
44. Marco, C.; Bello, A.; Faton, JG.; Garza, J. *Makromolek Chem.* 187 (1986) 177.
45. Liron, Z.; Cohen S. *J. Pharm. Sci.* 72 (1983) 499.
46. Errede, LA. *Macromolecules* 19 (1986) 1522.
47. Flory, PJ. Principles of Polymer Chemistry. Ithaca, New York: Cornell University Press; (1953).
48. Stockmayer, WH.; Fixman, M. *J. Polym. Sci.* 1 (1963) 137.
49. DipaolaBaranyi, G. Macromolecules 15 (1982) 622.
50. Ashworth, AJ.; Price, GJ. *Macromolecules* 19 (1986) 362.
51. Sperling, LH. Introduction to Physical Polymer Science. 3th ed. United States of America: John Wiley& Sons; 2001.
52. Koenhen, DM.; Smolders, CA. *J. Appl. Polym. Sci.* 19 (1975) 1163.
53. Mandel, M.; Varkevisser, FA.; Vantreslong, CJB. *Macromolecules* 15 (1982) 675.
54. Hansen, C.; Beerbower, A. Solubility parameters. In: Kirk- Orthmer (Ed.), Encyclopedia of Chemical Technology. A. Standen Editor, Supp. vol., 2nd ed. New York: Wiley- Interscience; 1971.
55. Thomos IB Sc, Applied Chemistry Dissertation, Torento Polytechnique 1975.
56. Darbye, JR.; Touchette, NW.; Sears, K. *Polym. Eng. Sci.* 7 (1967) 295.
57. Shultz, AR.; Glory, PJ. *J. Polym. Sci.* 15 (1955) 231.
58. Ravindra, R. *Carbohd. Polym.* 36 (1998) 121.
59. Small, PA. *J. Appl. Chem.* 3 (1953) 71.
60. Dunkel, M. *J. Phys. Chem.* 138 (1928) 42.
61. Bowden, ST.; Jones, WJ. *Phil. Mag.* 39 (1948) 155.
62. Hoftyzer, PJ.; van Krevelen DW. Paper No.IIIs-15, presented at International Symposium on Macromolecules of IUPAC, Lyden, 1970.
63. Hoy, KL. *J. Paint. Technol.* 42 (1970) 76.
64. van Krevelen, DW.; Hoftyzer, PJ. Properties of Polymers. Correlations with Chemical Structure. New York: Elsevier; 1972.
65. Barton, AFM. CRC Handbook of solubility parameters and other cohesion parameters. Boca Raton, FL: CRC Press; 1983.
66. van Krevelen, DW. *Fuel* 44 (1965) 229.
67. van Krevelen, DW.; Hoftyzer, PJ. *J. Appl. Polym. Sci.* 11 (1967) 2189.
68. van Krevelen, DW.; Hoftyzer, PJ. Properties of Polymers. Correlation with Chemical Structure. Amsterdam: Elsevier; 1976.
69. Lindvig, T.; Michelsen M.L.; Kontogeorgis, G.M. Thermodynamics of paint related systems with engineering models, AIChE J. 47 (2001) 2573.
70. Peppas N.A.; Brannon-Peppas L. *J Controlled Release* 40 (1996) 245.
71. Mikos, A.G.; Peppas N.A. *Biomat.*, 9 (1988) 419.

72. C.M. Hansen, Hansen Solubility Parameters. A User's Handbook, CRC Press, Boca Raton, FL, 2000.
73. E. Samios, R. K. Dart and J. V. Dawkins Polymer Vol. 38 No. 12, pp. 3045-3054, 1997 Preparation, characterization and biodegradation studies on cellulose acetateswith varying degrees of substitution
74. Heinze, T., & Liebert, T. *Macromolecular Symposia* 208 (2004)167.
75. Rajini, R., Venkateswarlu, U., Rose, C., & Sastry, T. P. *Journal of Applied Polymer Science* 82 (2001) 847.
76. pastarova, I.; Botto, RR.; Arisz, PW.; Boon, JJ.; *Carbohydra. Res.* 262 (1994) 27.
77. Sassi, J. F., Tekely, P.and Chanzy, H. *Cellulose* 7 (2000) 119.
78. Hernane S. Barud , Adalberto M. de Ara´ujo J´unior, Daniele B. Santos, Rosana M.N. de Assunc¸ ˜ao, Carla S. Meireles, Daniel A. Cerqueira, Guimes Rodrigues Filho, Cl´ovis A. Ribeiro, Younes Messaddeq, Sidney J.L. Ribeiro. *Thermochimica Acta* 471 (2008) 61.
79. Henry, LF. *Polym. Eng. Sci.* 14 (1974) 167.
80. Breitkreutz, J. J *Pharmaceut. Res.* 15 (1998) 1370.
81. Hoernschemeyer, D. *J Appl. Polym. Sci.* 18 (1974) 61.
82. Heinz, T. and Liebert, T. *Prog. Polym. Sci.* 26 (2001) 1689.

(2012) www.jmaterenvironsci.com