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Article

Some Aspects of Acetylation of Untreated and Mercerized Sisal Cellulose

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Este trabalho apresenta alguns aspectos da acetilação em LiCl/*N*,*N*-dimethylacetamida, DMAc de celulose de sisal nativa e mercerizada (sisal e M-sisal). A mercerização da fibra em solução de NaOH resulta nas seguintes alterações: decréscimo de 29.9 % no índice de cristalinidade; diminuição de 16.2% no grau de polimerização e aumento de 9.3% no conteúdo de α-celulose. Estudo com espalhamento de luz de soluções de sisal, M-sisal, celulose microcristalina e algodão mostrou que elas se apresentam na forma de agregados, com números médios de agregação de 5.2, 3.2, 9.8 e 35.3, respectivamente. A presença destes agregados afeta a acessibilidade à celulose durante sua funcionalização. Acompanhamento do grau de substituição, DS, de acetato de celulose em função do tempo, mostrou que o mesmo aumenta por um intervalo de tempo de 5 h, seguido por um decréscimo após 7 h. Possíveis razões para este decréscimo são discutidas. Como esperado, M-sisal apresenta um DS maior que a sisal nativa.

We report here on some aspects of the acetylation in LiCl/*N,N*-dimethylacetamide, DMAc, of untreated and mercerized sisal cellulose, hereafter designated as sisal and M-sisal, respectively. Fiber mercerization by NaOH solution has resulted in the following changes: 29.9% decrease in the index of crystallinity; 16.2% decrease in the degree of polymerization and 9.3% increase in α-cellulose content. A light scattering study of solutions of sisal, M-sisal, microcrystalline and cotton celluloses in LiCl/DMAc has shown that they are present as aggregates, with (an apparent) average aggregation numbers of 5.2, 3.2, 9.8, and 35.3, respectively. The presence of these aggregates affects the accessibility of cellulose during its functionalization. A study of the evolution of the degree of substitution, DS, of cellulose acetate as a function of reaction time showed an increase up to 5 h, followed by a decrease at 7 h. Possible reasons for this decrease are discussed. As expected, M-sisal gave a higher DS that its untreated counterpart.

Keywords: cellulose aggregation, cellulose acetylation, degree of cellulose acetate substitution, LiCl/DMAc

Introduction

Derivatization of cellulose, e.g., into esters and ethers is a subject of continuing interest because of the important applications of these products as fibers, filters, dialysis membranes etc.[1] Although cellulose can be isolated from several sources including plants, marine organisms and bacteria, its main source is (slowly regenerated) wood.[2] Therefore, there is an increasing interest in using dissolving pulps from fast-growing lignocellulosic sources, e.g., cotton, sisal and sugar cane. The amount of bagasse available from the last source is growing fast because of the increasing use of ethanol as a biofuel, additive for gasoline and (mineral) diesel oil and in the production of "biodiesel".[3] Sisal fiber, used in the present work, is potentially important because is easily cultivated; Brazil is one of the main sisal-producing countries.[4]

Industrially, cellulose esters of carboxylic acids are obtained under heterogeneous (solid/liquid) reaction conditions. The semi-crystalline nature of cellulose results in faster swelling, hence faster reaction in the amorphous regions than in their crystalline counterparts. Therefore, esters with degree of substitution, DS < 3 - in the anhydroglucose unit of cellulose, AGU - cannot be

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obtained directly under these conditions. The reason is that the products will be heterogeneous, due to more extensive substitution in the amorphous regions. Consequently, their relevant properties, e.g., solubility in organic solvents, and viscosity of the solutions thus prepared, may become non-reproducible.[2]

Most of these problems can be avoided by functionalization under homogeneous reaction conditions, HRC. Indeed, this scheme results in negligible degradation of the biopolymer, allows a better control of the reaction, and gives products whose properties, in particular DS, are reproducible. The most important characteristic of the HRC scheme is that its use permits obtaining esters of any DS directly, *i.e.*, not *via* partial hydrolysis of the tri-ester, as is done in the industrial process.[1] At first glance, the HRC scheme appears simple: the polymer is activated, dissolved in an appropriate solvent (strong electrolyte/dipolar aprotic solvent or an ionic liquid),[5] and then submitted to derivatization. Alternatively, polymer activation and dissolution is achieved in a single step.[6] This simplicity, however, is deceptive because the cellulose solutions obtained, e.g., in LiCl/*N,N*-dimethylacetamide, DMAc, are not necessarily molecularly dispersed. They may contain aggregates of still ordered cellulose molecules. This aggregation, if it occurs, affects the accessibility of the hydroxyl groups of the AGU hence the targeted DS.[7-9] Consequently, the properties of cellulose, in particular its degree of polymerization, DP, index of crystallinity, Ic, and its concentration in LiCl/DMAc affect its state of solution, hence its derivatization. In summary, HRC scheme is promising for the synthesis of specialty products, e.g., cellulose mixed esters for dialysis membranes. Its complexity calls for a better understanding and optimization of the steps involved.

We report here the acetylation of untreated and mercerized cellulose from sisal, hereafter designated sisal and M-sisal, respectively, in LiCl/DMAc. Light scattering experiments were carried out on microcrystalline cellulose and cotton cellulose, hereafter designated as MCC and cotton, respectively. The following points were investigated: the effect of mercerization on the characteristics of sisal cellulose; the physical state of the celluloses dissolved in LiCl/DMAc, and effect of reaction time on the DS of the product.

Experimental

Materials

The reagents were purchased from Merck or Synth (São Paulo) and were purified as given elsewhere;[10] LiCl was dried for 3 h at 200 °C, cooled and used promptly. MCC, Avicel PH-101, was obtained from FMC (Philadelphia). Sheets of sisal and cotton were obtained from Lwarcel Cellulose (Lençóis Paulista, São Paulo) and Nitro Química S. A. (São Paulo), respectively. They were cut into strips and grounded in a water-cooled cutting mill (Thomas Scientific model 3383-L10, Swedesboro) against a 10 mesh stainless steel sieve. All cellulose samples were further sieved through a 100-200 mesh sieve (Fritsch Analysette 3 Spartan, Idar-Oberstein).

Mercerization of sisal

Cellulose powder, 10 g, was added to 500 mL of a cold (0 °C) 20% NaOH solution; the suspension was (mechanically) stirred for 1 h; the solid was filtered and washed with water until the filtrate was neutral, then air dried.

Characterization of celluloses

Standard procedures were employed for the characterization of celluloses; these are described here only briefly: (*i*) the viscosity-based average molecular weight, M_v was determined at 25 °C from the intrinsic viscosity of cellulose solution in Cuen/water (1:1, v/v),[11] by using shear-dilution Cannon-Fenske viscometer (Schott), inserted in Schott AVS 360 automatic viscosity determination equipment; (*ii*) the α-cellulose content was determined from the dry masses (3 h at 105 °C) of cellulose before and after treatment with 17.5% NaOH solution, at liquor ratio = 1:20, m/v;[12] (*iii*) X-ray diffraction of the cellulose samples was recorded by using Carl Zeiss Jena URD-6 X-ray diffractometer. The CuK radiation from the anode operating at 40 kV and 40 mA was monochromatized with a 15mm Ni foil. Ic, was calculated from equation (1):[13]

$$Ic = 1 - I_{min}/I_{max} \quad (1)$$

where I_{min} is the intensity minimum between 2q = 18° and 19°, and I_{max} is the intensity of the crystalline peak at the maximum between 2q = 22° and 23°.

Static light scattering

Solutions of cellulose containing 1, 2, 3, 4 and 5 g L^{-1} were prepared in 6% LiCl/DMAc, as follows: powdered cellulose (100-200 mesh) was conditioned at 23 ± 1 °C, and relative humidity of 50 ± 2% for 24 h; its water content was determined by mass after drying (3 h at 105 °C). An adequate amount of conditioned cellulose was weighted

into a round bottom flask to give, after drying, a 0.5% solution. The required amount of LiCl was weighted into the same flask, the latter was connected to a vacuum pump, the solid mixture was dried at 110 °C for 1 h, followed by addition of the required amount of DMAc to give final LiCl concentration (6%). The heat was turned off and the slurry was stirred overnight, a clear solution was obtained. The other cellulose concentrations were prepared from the previous one, by dilution with a 6% LiCl/DMAc solution. All samples were centrifuged at 11000 rpm for 90 min, then transferred to the (cylindrical) cells of the light-scattering equipment, Malvern 4700MW equipped with a 25 mW He/Ne laser light source (Malvern, Worcestershire).

The weight-averaged molecular weight of the dissolved cellulose, M_W, was calculated from equation (2):

$$K\,c/R_\theta = (1/M_W\,P_\theta) + 2\,A_2c \quad (2)$$

where K is an optical parameter, equation (3), R_θ is the Rayleigh ratio, A_2 is the second virial coefficient, "c" being the concentration of the solute molecule (cellulose, g cm^{-3}) and P_θ is the form (or particle scattering) factor.

$$K = 2\,\pi^2 n_o^2\,(dn/dc)^2 / N\,\lambda^4 \quad (3)$$

In equation (3), (n_o) is the refractive index of the solvent, N is Avogadro's number, dn/dc is the refractive index increment of the cellulose solution, λ is the wavelength of the incident light. The value of (dn/dc) was measured with Optilab 903 interferometric differential refractometer (Wyatt, Santa Barbara) operating at 633 nm. The scattering of the different cellulose solutions was measured as a function of the scattering angle, from 35 to 135°; the value of M_W was calculated from the inverse of the intercept, at "c" and $\theta = 0$, of the of Zimm plot, of $K\,c/R_\theta$ *vs.* $\sin^2(\theta/2)$.[14,15]

Solubilization of celluloses in LiCl/DMAc and its subsequent acetylation

Time-dependence of Ic

Sisal, 2 g, was suspended in 100 mL of DMAc and the suspension was mechanically stirred and heated to 150 °C. After reaching this temperature, three samples, each *ca*. 10 mL, were withdrawn. LiCl, 3.5 g, was added in one portion; the solution temperature was raised to 170 °C and 10% of the solvent volume was distilled off under reduced pressure; these two steps required 30 min. After withdrawing two more samples at 170 °C; the bath heating was discontinued; the solution temperature dropped to 40 °C; a final sample was removed at this temperature. All samples withdrawn were added to methanol, the precipitate filtered, washed with methanol, and dried under reduced pressure. Values of Ic of the resultant solid samples were calculated from X-ray diffraction data, *vide supra*.

The conditions for samples 1 to 3 were: temperature = 150 ºC; no LiCl; samples removed right after the suspension has reached 150 °C (time = 0) and after 30, and 60 min, respectively. Samples 4 to 7 were withdrawn after LiCl was added, 4 and 5 were withdrawn at 170 °C, at 90 and 120 min, measured relative to sample 1. Finally, sample 6 was removed at 40 °C; after 240 min from sample 1.

Cellulose acetylation in LiCl/DMAc

The biopolymer was dissolved in a solution of LiCl/DMAc by employing a modification of the published procedure.[6] A glass reactor, equipped with a thermometer, gas inlet for dry, oxygen-free nitrogen and a distillation condenser was employed. A suspension of cellulose (2 g) in 100 mL DMAc was heated to 150 °C and kept at this condition for 1 h. The required amount of LiCl was introduced, the temperature was raised to the b.p. of DMAc, and 10% of the initial solvent volume was distilled. The heat was turned off, and the slurry was stirred overnight, a clear lightly amber solution was obtained. The cellulose solution temperature was raised to 110 °C, acetic anhydride was added and the reaction was kept at this temperature for the required length of time. The product was precipitated in methanol, washed with the same solvent and dried at 60 °C, under reduced pressure.

Characterization of the products

The DS of cellulose acetates (± 0.05) was determined by ^{1}H NMR, by using Brucker AC-200 NMR spectrometer, as follows: the sample, 5 mg, was dissolved in 0.5 mL DMSO-d_6. Before analysis, a drop of trifluoroacetic acid was added, in order to shift the peak of any residual (OH) group to lower field (away from TMS). The value of DS was determined by integration of the peaks (1.93 to 2.15 ppm).[16] This calculation was further checked against the area of the protons of the AGU (7 protons, between 3.487 and 5.091 ppm).

Results and Discussion

Cellulose characterization

Mercerization of sisal results in removal of hemicelluloses and transformation of cellulose I → cellulose II.[2,17] This treatment has resulted in the following changes: 29.9% decrease in Ic % (from 77 to 54); 16.2% decrease in DP (from 648 to 543), and 9.3% increase in the α-cellulose content (from 0.86 to 0.94). Figure 1 shows

the SEM micrographs of sisal and M-sisal. Mercerization has led to a decrease of the fiber cross section, and smoothing of its outer surface. That is, the transformation cellulose I → cellulose II is not only irreversible at the crystallographic level, but also at the morphological level, in agreement with results of other workers,[18] and with our recent data on mercerization of cotton and sisal fibers.[19] Equally important, mercerization leads to modifications in the biopolymer supra-molecular structure that are relevant to solvent uptake and subsequent biopolymer functionalization, e.g., a decrease in the size of the crystallites[20] an increase in pore volume due to expansion of the pores and unification of adjacent ones,[21] and increase in the degree of disorder of the hydroxymethyl groups.[22]

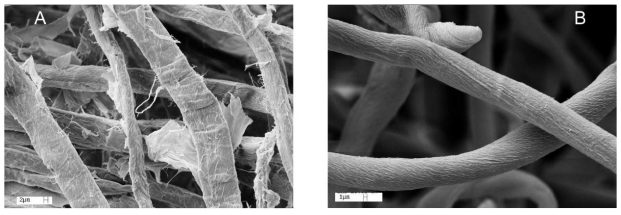

Figure 1. SEM micrographs: (A) sisal (× 2000); (B) M-sisal (× 5000).

Physical state of dissolved celluloses

Obtaining a clear cellulose solution is a necessary, but not sufficient condition to obtain the targeted DS. The reason is that isotropic cellulose solutions in LiCl/DMAc most probably contain biopolymer aggregates, whose accessibility are less than that of molecularly dispersed cellulose chains.[8] Therefore, we have investigated the state of aggregation of sisal and M-sisal in LiCl/DMAc, and compared the results obtained with those of MCC and cotton in the same solvent. Table 1 shows the values of M_V and M_W of celluloses, along with the radius of gyration, RG.

Table 1. Viscometric (M_V) and Weight (M_W) average molar masses (g mol^{-1}), degree of polymerization (DP), aggregation numbers and radius of gyration (RG) of celluloses in LiCl/DMAc

Sample	M_V (DP)	M_W	Apparent aggregation number	RG/nm
Sisal	105000 (648)	551850	5.2	68
M-Sisal	88000 (543)	284400	3.2	66
MCC	24300 (150)	238349	9.8	62
Cotton	137862 (851)	4868058	35.3	222

We take the ratio of M_W/M_V as "apparent" aggregation number of cellulose chains in LiCl/DMAc, column 4 of Table 1. We have employed the term apparent because of the different cellulose-solvent interactions in both experiments; namely LiCl/DMAc and Cuen, for M_w, and M_v, respectively (recall that cellulose solutions in Cuen are molecularly dispersed).[23] As shown in the latter, all celluloses form aggregates in solution. Removal of hemicelluloses leads to a decrease in tendency of aggregation, as shown for sisal and its mercerized counterpart.[24] The value of RG usually depends on the form of the particle in solution and, for macromolecules, increases as a function of increasing M_W, as shown in the last column of Table 1. The structure of the aggregates has been described in terms of "fringed micelles", whose dimensions are related to RG by equation (4), where (L) and (r) refer to the length and cross section area of the micelle, respectively, with the central part approximately cylindrical, as shown schematically in Figure 2.[9,25]

$$R_G = [(L^2 + 6r^2)/12]^{1/2} \quad (4)$$

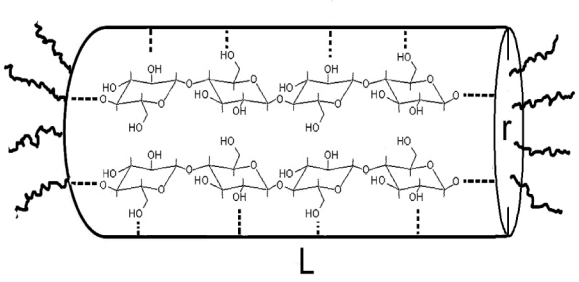

Figure 2. The "fringed micelle" model of cellulose aggregates in LiCl/DMAc.

The result for cotton is expected because of its large DP. This large apparent aggregation number bears on its accessibility in chemical reactions. In fact, many workers use mercerized cotton in order to approach the DS targeted.[1] Surprisingly, the relatively small MCC forms particles whose apparent aggregation number is higher than that of sisal and M-sisal, hence the value of (r) is probably higher for the former. On the other hand, the micelles of sisal have larger (L) since the M_W of the monomer is larger. The effects of both structural variables on RG compensate, resulting in RG that is not substantially different for both types of cellulose. These results show the complexity of the HRC scheme. MCC is a relatively small cellulose, hence it is expected to be more accessible (*i.e.*, more reactive) than relatively large, fibrous celluloses. This difference in reactivity depends, however, on the state of aggregation of the biopolymer. That is, a part of the high reactivity of MCC may be offset by a decrease in accessibility, due to its aggregation.

Effect of Dissolution of sisal in LiCl/DMAc on the crystallinity of the biopolymer

As given in Experimental, aliquots of the suspension of cellulose in LiCl/DMAc were withdrawn, the biopolymer was precipitated, dried and its Ic determined (Figure 3). These results can be explained as follows: the changes that occur during the initial drop of Ic (0, 30 and 60 min) include solvent penetration into the fiber wall; breaking of the fiber and fibril structures; formation of fragments and dissolution of a part of amorphous cellulose. Some intra-crystalline swelling, leading to an increase in the accessibility of the crystalline regions most certainly occur during this initial stage.[26] The value of Ic decreases only slightly when the temperature was raised from 150 to 170 °C (90 min). The origin is that the enthalpy of solution of cellulose is the sum of several steps; so that the overall process is exothermic.[27,28] That is, cellulose dissolution by complexation with LiCl/DMAc becomes unfavorable at higher temperatures, and is favored at lower temperatures, as shown by the second drop in Figure 3 (40 °C, 240 min).[29] The relevance of Figure 3 is that it shows that heating of cellulose in LiCl/DMAc, to 150 °C, then to 170 °C, and finally cooling to 40 °C is advantageous, because it leads to a noticeable decrease the crystallinity, hence a corresponding increase in accessibility of the biopolymer, a prerequisite for obtaining the targeted DS.

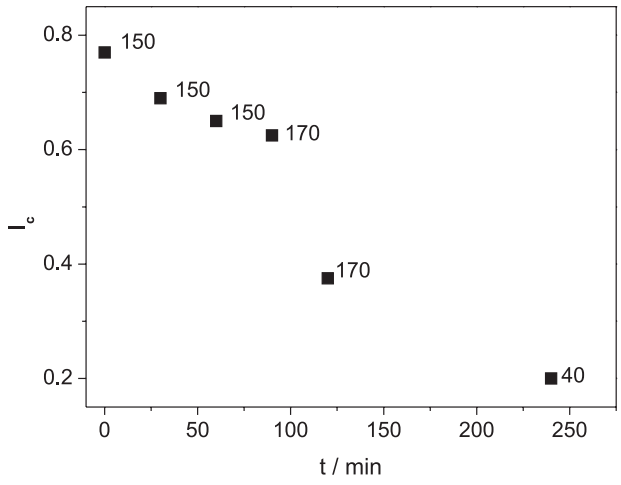

Figure 3. Dependence of Ic on time and temperature of sisal-LiCl/DMAc suspension. The "zero" time was taken when the temperature of the suspension reached 150 °C; the temperatures (in °C) are indicated in the graph.

Figure 4 shows the evolution of DS as a function of reaction time during 7 h. The targeted DS was 2, *i.e.*, 6 mol of acetic anhydride/AGU were employed. As shown, DS increases slowly until 3 h, then faster up to 5 h, followed by a decrease when the reaction was extended to 7 h. An experiment was carried out in order to independently verify this DS decrease. Briefly, cellulose acetate of known DS was heated with acetic acid in LiCl/DMAc, under the same conditions employed in the acetylation experiment (see Experimental) and its (final) DS was determined. An ester sample was prepared from sisal, by using excess acetic anhydride in order to achieve a DS = 2.0.[30,31]. One mol of ester was heated in LiCl/DMAc to 160 ºC; kept at this temperature for 2 h; the solution cooled to room temperature and was kept under agitation overnight. Two moles of glacial acetic acids were then added, the solution temperature was increased to 110 ºC; agitation was continued at this temperature for additional 2 h; the ester precipitated and purified. Its (low) DS, 0.4, confirm the result depicted in Figure 4.

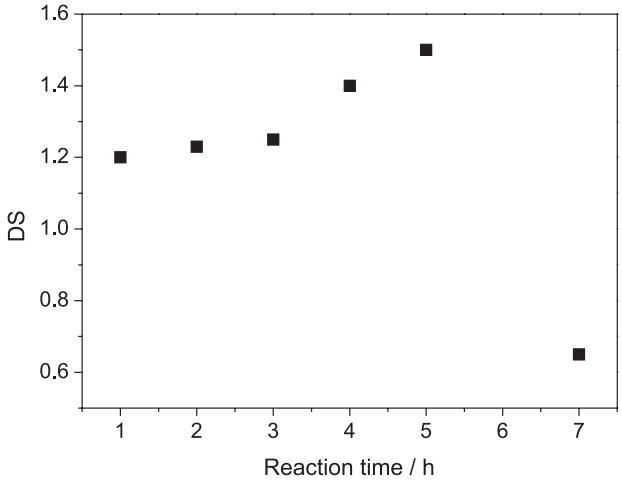

Figure 4. Evolution of DS of cellulose acetate of M-sisal in LiCl/DMAC as a function of time.

Several explanations can be advanced in order to explain this decrease: (*i*) parallel acid-catalyzed ester hydrolysis by adventitious water; (*ii*) LiCl-mediated de-acetylation; (*iii*) degradation of cellulose by a side reaction. Considering (*i*), we have shown that distillation of 25% DMAc removes *ca*. 56% of the water present in the cellulose/LiCl-DMAc solution.[32] A simple calculation based on 2 g cellulose (12.3 mmol) whose initial water content is 5% shows that 2.4 mmol of water is not removed; this can lead to hydrolysis of *ca*. 20% of cellulose acetate. Additional adventitious water may come from the very hygroscopic LiCl. This explanation, however, is unlikely because there is no obvious reason why water should react faster with cellulose ester than with (more reactive) acetic anhydride.

Another possibility (*ii*) is shown in the scheme depicted in Figure 5, where attack of acetic acid on the cellulose ester is LiCl-mediated to give a tetrahedral intermediate from which protonated cellulose, or acetate anion may leave; the

first leads to de-acetylation. Provided that the intial step is operative (LiCl-assisted attack of acetic acid on cellulose ester), the scheme shown below is in agreement with the fact that the pKa of protonated alcohols (a model for protonated cellulose) is relatively low, *ca*. –2.[33]

With regard to (*iii*), it is known that heating cellulose in DMAc at the b.p. of the latter leads to yellowing of the biopolymer, due to the formation of chromophors, including dehydroacetic acid, isodehydroacetic acid and dimethyl-γ-pyrone.[34] Using ^{1}H NMR and a trapping experiment (of the intermediate), it has been shown that this is due to enolization of DMAc, the intermediate formed (CH_2=C(OH)N(CH_3)$_2$) may lose water, in an (acetic) acid-catalyzed step to form *N,N*-dimethylketeniminium ion (CH_2=C=N$^+$(CH_3)$_2$). The formation of the DMAc-originated cation, and its precursor is accelerated at temperatures > 90 °C,[33] *i.e*., below the temperature used for acetylation of cellulose. This cation is an extremely reactive electrophile, capable of random cleavage of the bonds present, e.g., between AGUs, or between an AGU and the acetate group. This results in rapid changes in the molecular weight distribution of cellulose,[34] and presumably a decrease in DS. We plan to investigate further the reason for the decrease in DS as a function of time. Finally, the DS of M-sisal was higher, 1.5, than that of untreated sisal, 1.2, because of the higher accessibility of the former, *vide supra*.

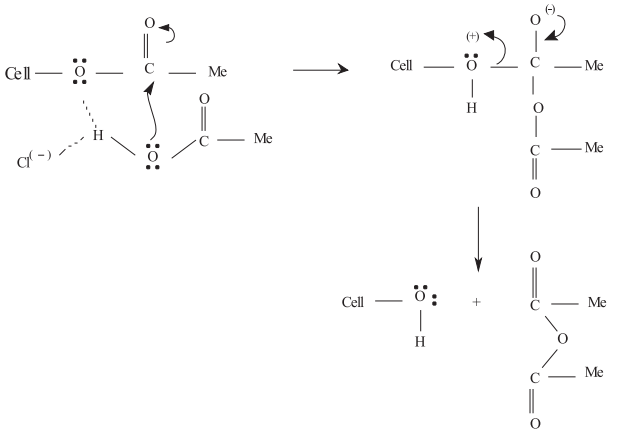

Figure 5. Scheme for LiCl-mediated de-acetylation reaction.

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