

Supplementary material

A physical organic chemistry approach to dissolution of cellulose: effects of cellulose mercerization on its properties and on the kinetics of its decrystallization

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**Dedicated to Professors Rita H. Rossi, Julio C. Podestá, Manuel González Sierra,
and Oscar S. Giordano**

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Calculations: Calculations of the rate constants and activation parameters for the decrystallization of cellulose.

Solvent-induced decrystallization of cellulose can be monitored under *non-isothermal* conditions by following the decrease of I_c as a function of time (t) and temperature (T).¹ In the presence of a constant $[LiCl]$, this process can be treated as a pseudo-first-order reaction (Eq. 1), and the rate of reaction can be obtained by equation 2:



$$v = -\frac{d[A]}{dt} = k[A] \quad (2)$$

Where v = reaction rate and k = rate constant; the term "A" refers to the crystalline region. The latter is proportional to I_c ; Eq 2 can be expressed as:

$$v = -\frac{dI_{c_t}}{dt} = kI_{c_t} \quad (3)$$

Where I_{c_t} represents the value of I_c at time (t).

Because all reactions were carried out under non-isothermal conditions, the values of k and I_{c_t} are also dependent on (T). It is then necessary to know the values of k for each time/temperature, designated as $k(t)$. These were calculated from $(I_{c_0} - I_{c_t})$ vs. (t), as shown for mercerized linters in Figure S1-a. The slope gives the value of $d(I_{c_0} - I_{c_t})/dt$, which when divided by I_{c_t} (Eq.3) provides the respective values of $k(t)$.²⁻⁴ The curves obtained for the other celluloses (figures not shown) are similar. Values of the temperature at any time, $T(t)$, were obtained from the *cooling curves* [T (degree Kelvin) vs t (s)], as shown in Figure S1-b.

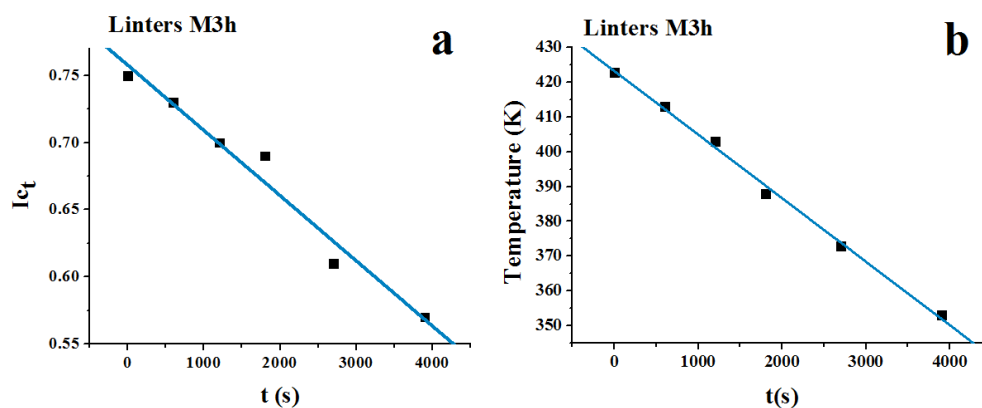


Figure S1. Dependence of $(I_{c_0} - I_{c_t})$ on time during the decrystallization of linter sample M3h in LiCl/DMAc, (a); relationship between the cooling rate and time during the decrystallization of the same sample, (b).

From the values of $k(t)$ and $T(t)$ it was possible to calculate the activation parameters for the decrystallization of celluloses, by using the Eyring equation^{1, 5, 6}, adapted to non-isothermal conditions; see Figure S2:

$$\ln[k(t)h / k_B T(t)] = \Delta S^\ddagger / R - \Delta H^\ddagger / RT(t) \quad (4)$$

Where h is Planck's constant [$6.63 \times 10^{-34} \text{ J s}^{-1}$], k_B is Boltzmann's constant [$13.81 \times 10^{-24} \text{ JK}^{-1}$], $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and time is given in seconds. From $\ln[k(t)h / k_B T(t)] \times 1/T(t)$ (Figure S2) straight lines were obtained whose slope and intercept are $\Delta H^\ddagger / R$ and $\Delta S^\ddagger / R$, respectively.

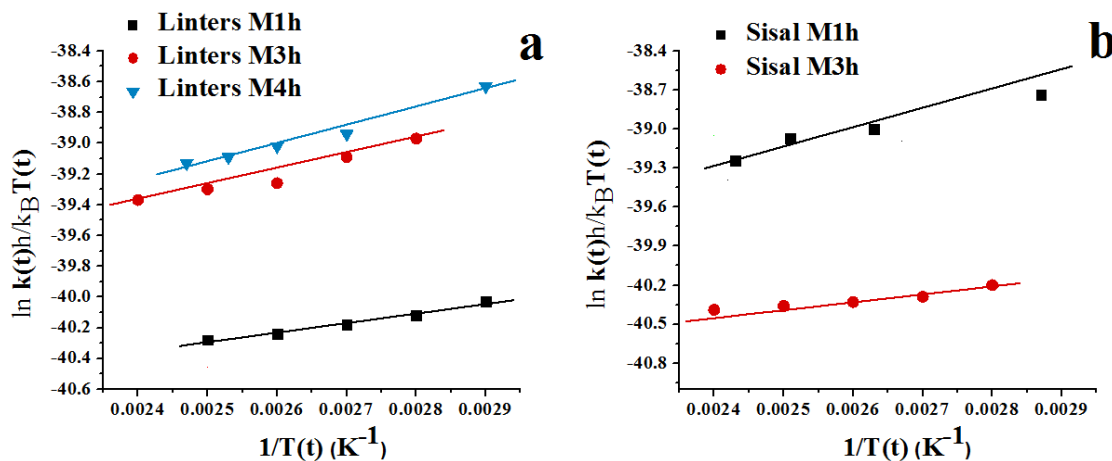


Figure S2. Eyring plots for biopolymer decrystallization in LiCl/DMAc. The plots shown are for mercerized linters, (a), and mercerized sisal, (b).

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