# **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 decrystallinization of cellulose can be monitored under *non-isothermal* conditions by following the decrease of Ic as a function of time (t) and temperature (T).<sup>1</sup> 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:

$$A \rightarrow B$$
 (1)

$$v = -\frac{d[A]}{dt} = k[A]$$
<sup>(2)</sup>

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:

$$v = -\frac{dlc_{t}}{dt} = klc_{t}$$
(3)

Where  $Ic_t$  represents the value of Ic at time (t).

Because all reactions were carried out under non-isothermal conditions, the values of k and Ic<sub>t</sub> 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  $(Ic_0 - Ic_t)$  vs. (t), as shown for mercerized linters in Figure S1-a. The slope gives the value of  $d(Ic_0 - Ic_t)/dt$ , which when divided by Ic<sub>t</sub> (Eq.3) provides the respective values of k(t).<sup>2-4</sup> 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  $(Ic_0-Ic_t)$  on time during the decrysatllization 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 decrystallinization of celluloses, by using the Eyring equation<sup>1, 5, 6</sup>, adapted to non-isothermal conditions; see Figure S2:

 $\ln[k(t)h / k_{\rm B}T(t)] = \Delta S^{\neq}/R - \Delta H^{\neq}/RT(t)$ (4) Where *h* is Planck's constant [6.63x10<sup>-34</sup> J s<sup>-1</sup>], k<sub>B</sub> is Boltzmann's constant [13.81x10<sup>-24</sup> JK<sup>-1</sup>], R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup> and time is given in seconds. From ln[ k(t)h / k<sub>B</sub>T(t) ] × 1/T(t) (Figure S2) straight lines were obtained whose slope and intercept are  $\Delta H^{\neq}/R$  and  $\Delta S^{\neq}/R$ , respectively.



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

## References

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