



# Time temperature superposition of the dissolution of cellulose fibres by the ionic liquid 1-ethyl-3-methylimidazolium acetate with cosolvent dimethyl sulfoxide

James E Hawkins, Yunhao Liang, Michael E Ries\*, Peter J Hine

School of Physics and Astronomy, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK

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## ABSTRACT

The dissolution of cellulosic flax fibres in the ionic liquid 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) with cosolvent dimethyl sulfoxide (DMSO) has been studied. The fibres were submerged in the ionic liquid/DMSO mixtures at different temperatures for a range of dissolution times, then coagulated in water. After drying, cross sections of the fibres were analysed using an optical microscope, which was used to track the fraction of coagulated fibre. The temperature dependence of this coagulated fraction is found to follow an Arrhenius equation with a single activation energy of  $100 \pm 10$  kJ/mol. This value is, remarkably, independent of the weight fraction of DMSO used. This work quantifies the composition for the peak dissolution rate, which occurs at an equal weight fraction of DMSO and [C2mim][OAc]. Finally, this study reveals an equivalence between time, temperature and DMSO weight fraction in the dissolution of flax fibres.

## Introduction

The dissolution of cellulose is an area of great interest both academically and industrially. The pulping industry uses an acidic solution in conjunction with heat and pressure to process wood chips and bark. The creation of cellophane involves the dissolution of cellulose and areas within bio-composite science require the partial dissolution of cellulose fibres in the preparation of eco-friendly composites (Chen et al., 2016; Chen et al., 2020). Dissolution is crucial, as unlike many petroleum-based polymers, cellulose does not melt but instead decomposes at elevated temperatures (Das, 1981).

Cellulose does not dissolve in common solvents - resulting in the need to find alternatives. Though dissolution is not fully understood, there is a consensus that solvents must be able to disrupt the strong intermolecular interactions, (both h-bonds and hydrophobic forces) within the crystal (Lindman et al., 2017; Bocek, 2003). The earliest mention of the dissolution of cellulose containing materials dates back to 1846, when Christian F. Schonbein discovered the solubility of cellulose nitrate (Liebert et al., 2010). This was followed by English chemists Charles F. Cross, Edward J. Bevan and Beadle Clayton as they used aqueous sodium hydroxide in the presence of carbon disulphide as a means of dissolving wood pulp (Huber et al., 2012). This procedure eventually became known as the Viscose process and is widely used commercially to this day, despite the corrosive nature of the solvents used.

With the advent of ionic liquids (IL's), a new, 'environmentally friendly' method of cellulose dissolution has been established (Swatloski et al., 2002; Ghandi, 2014). IL's are salts in the liquid state below 100 °C and many have shown the ability to dissolve cellulose without the need for pre-treatments such as swelling. IL's also have low vapour pressure and are potentially recyclable (Liu et al., 2015; Ghandi, 2014). These viscous liquids consist of a large, organic cation in conjunction with a smaller anion and were first synthesised by Paul Walden in 1914 (Plechova & Seddon, 2008). Other reasons for the popularity of these liquids include their impressive solvating potential, (Welton, 1999) thermal stability (Meine et al., 2010) and tuneable properties via suitable choices of anion/cation (Ahrens et al., 2009). Much work has shown how the viscosities of ionic liquids can be drastically changed with alterations in the size of the anion, (Green et al., 2017) or via the addition of even small amounts of water or carbohydrates (Ries et al., 2018; Ries et al., 2014). The earliest mention of cellulosic dissolution using a molten salt (N-alkylpyridinium chloride) occurred in 1934, (Pinkert et al., 2009) though this does not qualify as an IL based on Walden's definition, due to its high melting point. It is only recently (2002) that Swatloski et al first published results describing the dissolution of cellulose using a selection of methyl-imidazolium based ionic liquids (Swatloski et al., 2002). This seminal work has since influenced many publications and review papers (Huber et al., 2012).

\* Corresponding author.

E-mail addresses: [py11jeh@leeds.ac.uk](mailto:py11jeh@leeds.ac.uk) (J.E. Hawkins), [pyyl@leeds.ac.uk](mailto:pyyl@leeds.ac.uk) (Y. Liang), [M.E.Ries@leeds.ac.uk](mailto:M.E.Ries@leeds.ac.uk) (M.E. Ries), [P.J.Hine@leeds.ac.uk](mailto:P.J.Hine@leeds.ac.uk) (P.J. Hine).

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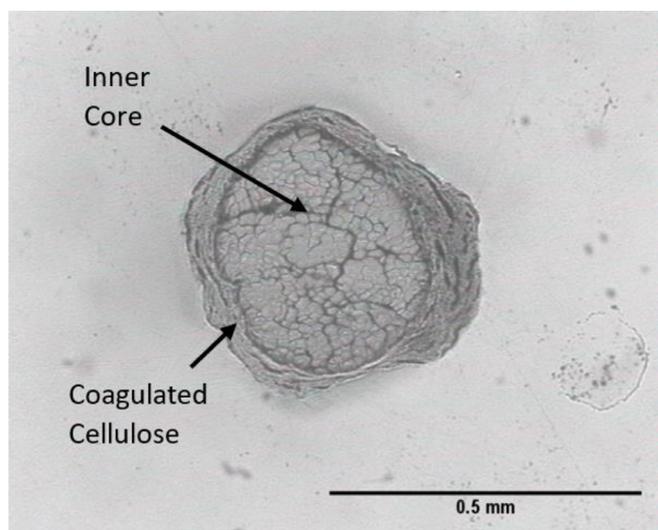
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Dimethyl Sulfoxide (DMSO), discovered in the latter half of the 19<sup>th</sup> century is a by-product from wood pulp created during the production of paper (Capriotti & Capriotti, 2012). It is a polar, aprotic solvent, colourless and miscible in water. Widely used in biomedical fields for the cryopreservation of cells and as a penetration enhancer during topological treatments (Gad & Sullivan, 2014), it has also been shown to be an excellent solvent for many organic and polymeric compounds due to its high polarity (Zhao et al., 2015). Though DMSO cannot dissolve cellulose, its low cost, low toxicity and low viscosity make it a great candidate for a co-solvent. DMSO is believed to improve the solvation capacities of ionic liquids by facilitating mass transport through decreasing the viscosity of the system (Andanson et al., 2014). Others have suggested that DMSO is, however, able to interfere with the interactions between anions and cations (Xu et al., 2013). Radhi Et al. reports that the addition of DMSO reduces the difference between diffusivities of the cation and anion in [C2min][OAc]. The ratio of the cation to anion diffusivities tend to unity around 0.6 mole fraction of DMSO and at higher DMSO concentrations, the diffusivity of the anion is shown to be faster than that of the cation (Radhi et al., 2015). It is however unknown as to whether such behaviour plays an appreciable role in the context of cellulose dissolution.

The work presented here can be closely tied to the series of papers published by Nevard et. al on the swelling and dissolution of cellulose fibres in a range of solvents (Céline Cuissinat et al., 2008b, 2008a; Céline Cuissinat & Navard, 2006a, 2006b; Cuissinat & Navard, 2008). Solvent mixtures in this series include aqueous NMMO along with a host of additives such as urea and zinc oxide, as well as multiple ionic liquids. The quality of the NMMO as a solvent is shown to be a function of water content, with a large amount of water resulting in poor solvating properties. Within the NMMO system, two main mechanisms of dissolution are reported- ‘ballooning’ and ‘disintegrating’, seen with high- and low-quality solvents respectively. The ‘ballooning’ dissolution mechanics are reported to be entirely due to the structure of the cellulose fibres and not the type of solvent, as the same phenomenon is seen when using both aqueous NMMO and ionic liquids. It was found that plant, cotton and wood fibres, as well as nitrocellulose and xanthene all display similar dissolution mechanics in these systems. The work presented in this paper follows on from the work conducted by Nevard et al, but with an emphasis on the temperature dependence of dissolution. Our hypothesis is that the dissolution of flax fibres in an ionic liquid will obey time-temperature superposition.

## Materials and methods

The solvent used was 1-ethyl-3-methylimidazolium acetate purchased from Sigma-Aldrich with a purity of >95%, as this particular ionic liquid’s ability to dissolve cellulose is well documented (Liu et al., 2019; Ding et al., 2012). Flax fibres, in the form of continuous yarn with a diameter of approximately 0.5 mm were purchased from Airedale Yarns and used as the source of cellulose. Prior to dissolution, fibres were wound around a PTFE picture frame of dimensions 5 cm × 5 cm. The frame was then submerged in a bath of IL/DMSO which was in turn, placed in a Leybold Sogevac vacuum oven capable of pumping down to 0.5 mbar. The [C2mim][OAc] was preheated to the desired temperature prior to dissolution. The vacuum was maintained during the dissolution process in order to prevent the absorption of atmospheric moisture by the IL, as multiple studies have shown substantial interactions between water and [C2mim][OAc] (Hall et al., 2012). These interactions result in a reduction in the dissolving capabilities of ionic liquids, even at water concentrations as low as 2–5% (Olsson et al., 2014; Tran et al., 2003; Le et al., 2012). Upon exiting the oven, the fibres, still wound around the frame, were placed in a running water bath for 24 h at room temperature. Finally, once removed from the water bath, fibres were left to dry at room temperature for a further 24 h before being cut free from the frame. Schematic of apparatus can be seen in SI 1.



**Fig. 1.** A partially dissolved fibre, displaying both raw cellulose (inner core) and coagulated cellulose (outer layer).

### Optical microscopy

Optical micrographs were attained using an Olympus BH2 microscope to analyse a cross section of each sample. Partially dissolved fibres were embedded vertically within an epoxy resin mould, which was ground down to the fibre surface and polished prior to imaging. Software (ImageJ) was used to determine the ratio between raw and coagulated cellulose, making use of the noticeable visual difference between the two. (Shown in Fig. 1.)

### Cosolvent

The cosolvent (DMSO) was mixed into the IL with a magnetic stirrer for 10 minutes prior to use. Three cosolvent concentrations were used: 20%, 50% and 75% by weight.

### Controlling water content

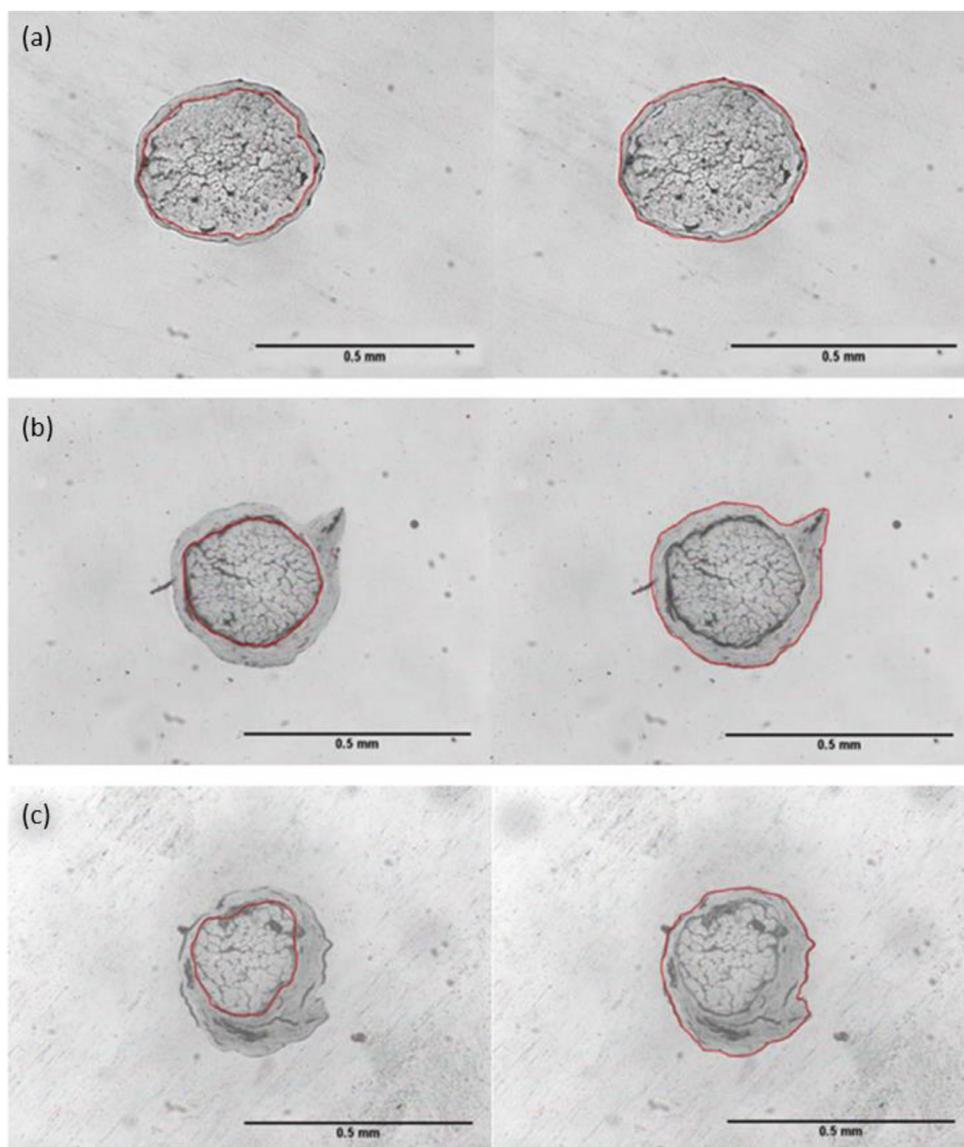
Most ionic liquids are hygroscopic and the dissolving capability of an IL can be drastically reduced by even a small amount of water (Cuadrado-Prado et al., 2009). In order to limit the uptake of atmospheric moisture, a vacuum oven was used during dissolution. A Bruker 400 MHz Avance II NMR Spectrometer was used before and after the dissolution process to determine the water content of the solvent bath, which was found to remain below 0.5%. The cosolvent DMSO exhibits a much higher vapor pressure than the IL and would evaporate under vacuum as a result. For this reason, the vacuum was replaced with a nitrogen atmosphere when using the cosolvent.

## Results and discussion

### Optical data

Optical microscopy allowed for imaging of both raw and partially dissolved fibres. Raw fibres are comprised of many individual fibrous bundles, packed tightly together. This tight packing and lack of free volume may act to slow the penetration of a solvent deep into the core. Images of raw fibres can be found in SI 2.

Upon processing, two distinct regions are visible in the optical micrographs. The undissolved inner core can be seen to be surrounded by a notably different outer layer, see Fig. 1. This outer layer is made of cellulose that has undergone the dissolution and coagulation process



**Fig. 2.** Image showing how the boundaries between raw and coagulated cellulose were determined. The inner boundary is shown on the left and the outer on the right. Fibres shown were dissolved at 50 °C for a) 0.5h, b) 2h, and c) 6h. Scale bar length 0.5 mm.

(Confirmed to be a combination of the cellulose II crystal and amorphous material via Wide Angle X-ray Diffraction. Data to be published at a later date).

The clear boundaries between core and coagulated material, as well as coagulated material and exterior can be established and measured. Software was used to trace out each boundary and the ratios between inner and outer boundaries were averaged across three different samples dissolved under identical conditions. The area enclosed within these boundaries is used to determine the relative amounts of coagulated and un-coagulated material, see Fig. 2.

The outer layer is referred to as the ‘Coagulation Fraction’ (CF) and is calculated by the following expression:

$$CF = A_C / A_T \quad (1)$$

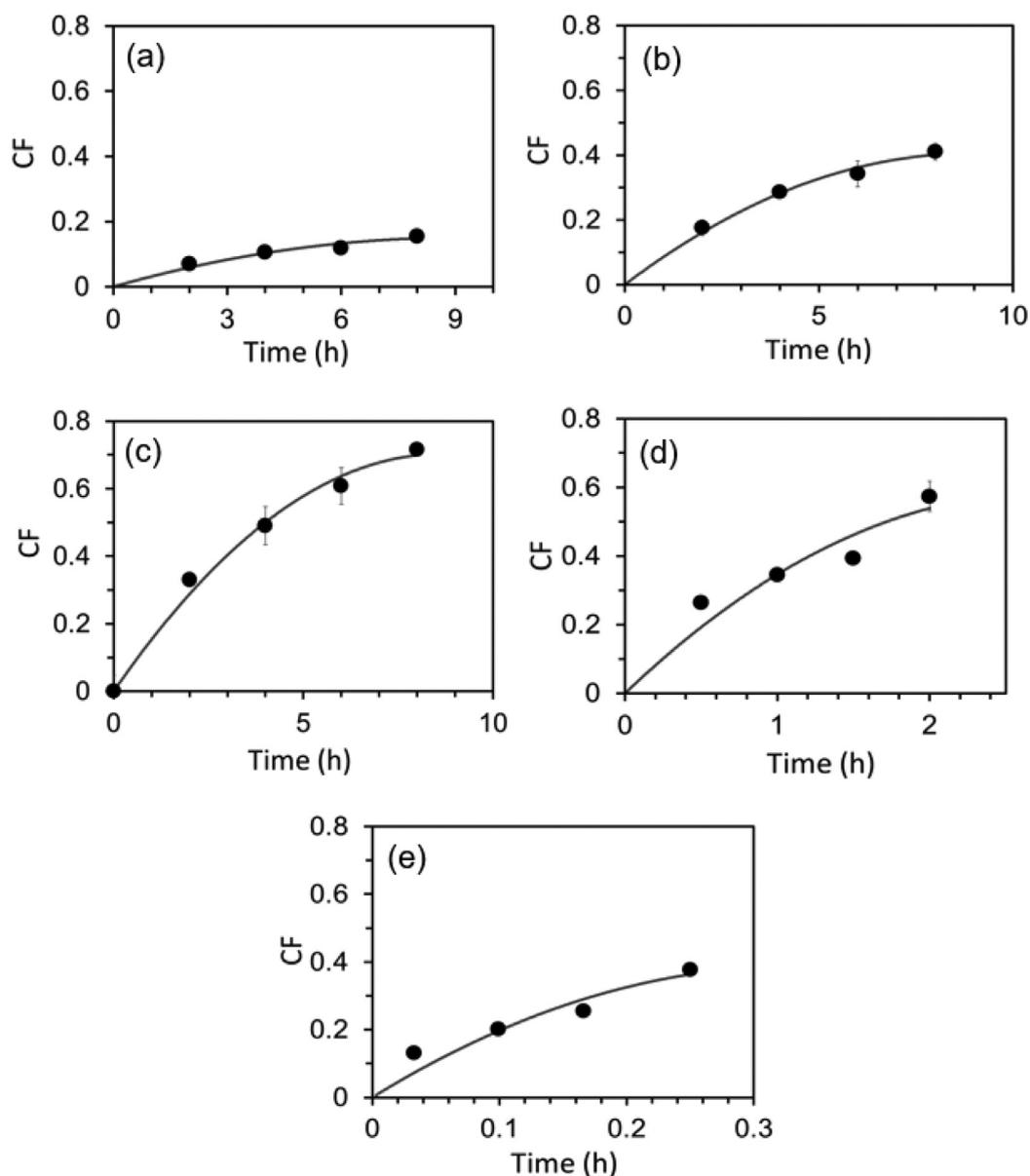
where  $A_C$  is the cross-sectional area of the coagulated cellulose and  $A_T$  the total cross-sectional area of the fibre (both coagulated and raw).

As expected, the coagulated fraction increases in size as a function of both dissolution time and temperature. First, the coagulated material forms quickly and roughly symmetrically around the core before its growth is slowed at longer times. This slowing is thought to be caused by the outer layer acting as a protective barrier between the inner, raw cellulose and the ionic liquid- hindering the dissolution process. The

appearance of the core remains largely unchanged, suggesting that the ionic liquid is acting predominantly at the fibre surface.

Fig. 3 shows the coagulation fraction growth with time. The CF is never seen to rise above 0.8 due to the limitations of the measurement technique; fibres dissolved by over 80% do not contain enough material to stay attached to the frame.

All data in Fig. 3 can be seen collated in Fig. 4, whereby a master curve is formed. To form this master curve, each data set was independently scaled in the time domain by a factor  $\alpha(T)$ , as is commonplace in rheological studies when dealing with time-temperature-superposition (TTS). The reference temperature, chosen to be 50 °C was fit with a preliminary polynomial function to give a visual guide for the shifting of other data sets. All data sets were then shifted towards this fit by eye and the amount of shifting in natural logarithmic time ( $\ln t$ ) is given by the value  $\ln(\alpha(T))$ . Lastly, a final polynomial function was fit to all data sets and the R-squared value between this function and each subsequent data set was computationally maximised via the manipulation of  $\ln(\alpha_{30})$ ,  $\ln(\alpha_{40})$ ,  $\ln(\alpha_{60})$  and  $\ln(\alpha_{70})$ . Fig. 4(b) shows each data set expressed in  $\ln$  time before the shift factor is applied. Following this, Fig. 4(c) documents how the data appears as the shift factors are applied in turn. Upon the shifting of all data sets, the master curve, seen in Fig. 4(d) is formed.



**Fig. 3.** The coagulated fraction (CF) of cellulose as a function of time at various dissolution temperatures. Graph (a): 30°C, (b): 40°C, (c): 50°C, (d): 60°C and (e): 70°C. Polynomial fits used to guide the eye. Error bars included, though may be smaller than data points.

The master curve shown in Fig. 4(d) provides evidence of time-temperature superposition in this system. Optical micrographs also documenting the interchangeability of time and temperature can be found in SI 3 and 4. The shift factors (tabulated in SI 5) used to generate the master curve are plot against the inverse of their respective temperatures in Fig. 5. The linear nature of the data seen in Fig. 5 is indicative of a system obeying an Arrhenius law, thus, a corresponding activation energy ( $E_a$ ) can be determined via:

$$\alpha(T) = A e^{-\frac{E_a}{RT}} \quad (2)$$

Where  $A$  is the pre-exponential factor,  $E_a$  the activation energy,  $R$  the gas constant and  $T$  temperature.

Others have shown Arrhenius behaviour in relation to cellulosic dissolution; for example when analysing the decrystallisation of microcrystalline cellulose in phosphoric acid (Zhang et al., 2009). Time temperature superposition in a similar system has also recently been documented by Chen et. al, whereby they quote: “The rising of tempera-

ture was found to amplify both the dissolution and swelling phenomena but did not change the observed behaviour (of cellulose fibres in [C2mim][OAc])” (Chen et al., 2020a). Within their work, they also independently document the clear boundaries seen between a fibrous core and a swollen exterior.

The activation energy was found to be  $100 \pm 10$  kJ/mol from the best fitted line in Fig. 5. This is thought to relate to the energy barrier to be overcome in separating cellulose molecules from their position in the crystal lattice. Wang et al. report a similar value for the activation energy of cellulose dycrystallisation when using sodium hydroxide and urea as solvents, at 62 kJ/mol (Wang & Deng, 2009). The enthalpy of cellulose solvation in [C2mim][OAc] has also been recently documented by Brehm et al, whereby computer simulations reveal a value of 96.4 kJ/mol (Brehm et al., 2019). In other work, Brehm et al. also quote a range of cellulose solvation enthalpies existing between 75.5 and 93.4 kJ/mol when using other ionic liquids (Brehm et al., 2020).

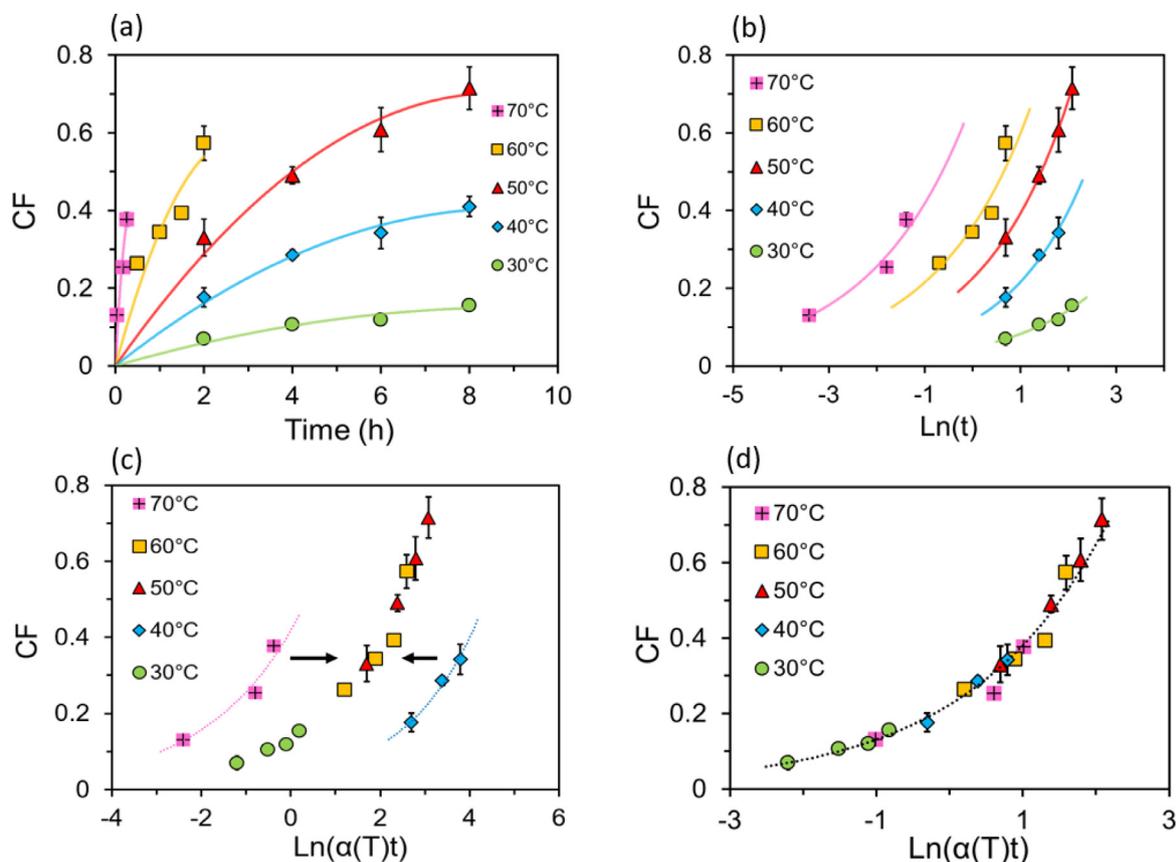


Fig. 4. a) Coagulated fraction (CF) as a function of dissolution time for all dissolution temperatures. b) CF as a function of dissolution time for all temperatures expressed in  $\ln$  time. c) Shifting process- moving the 40°C and 70°C data towards the 50°C data. d) Master curve showing the influence of both time and temperature on the coagulation fraction.

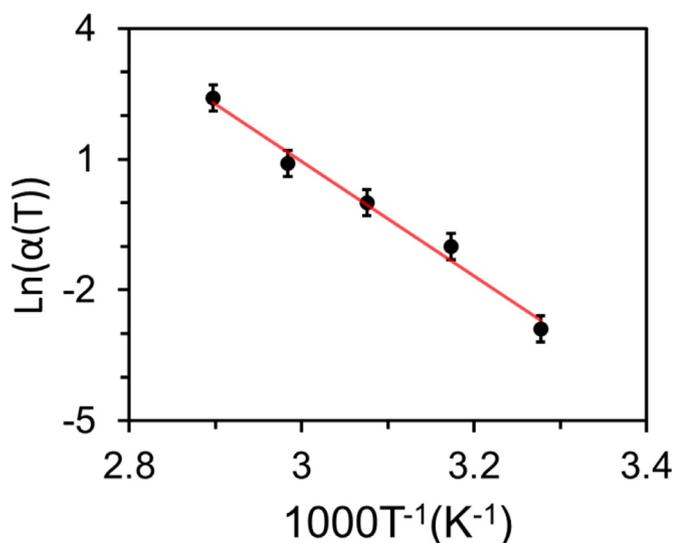


Fig. 5. Arrhenius plot showing the relation between shift factors  $\ln(\alpha(T))$  and temperature.

#### Addition of DMSO

DMSO was added as a cosolvent at various concentrations. In order to understand its effects on dissolution, fibres were again partially dissolved and photographed under a microscope. The most obvious difference in the IL + co-solvent system was the marked change in viscosity,

as DMSO has been shown to alter the viscosity of [C2mim][OAc] by up to two orders of magnitude (Radhi et al., 2015). In a similar system consisting of 1-ethyl-3-methylimidazolium chloride, DMSO and cellulose, Lu et al. found the viscosity activation energy to depend on cellulose concentration- ranging from 35 kJ/mol for the pure solvent to 75 kJ/mol at 10 wt. % of cellulose (Lu et al., 2015).

The dissolution mechanism seen in the IL with cosolvent system was found to remain the same as that of the pure IL system; fibres continue to dissolve from the outside in, with the formation of a dissolved and coagulated fraction appearing around the core. The main difference seen when using DMSO however, is the rate at which fibres dissolve, suggesting that the cosolvent is, in part, acting to alter the timescales of dissolution by reducing the solvent viscosity (Andanson et al., 2014; Chen et al., 2020a). A coagulation fraction master curve is constructed for each concentration of DMSO (see Fig. 6) by following the procedure outlined in Fig. 4.

Fig. 6 shows that time-temperature superposition also occurs in the system when using DMSO as a cosolvent. The shift factors used to create these curves can be used to calculate a corresponding activation energy for each co-solvent concentration, see Fig. 7. Quite remarkably, the activation energy did not depend on the weight fraction of DMSO, despite the rate of dissolution changing drastically, as shown in Fig. 8. The activation energies are remarkably constant across all cosolvent concentrations, with an average value of  $98 \pm 2$  kJ/mol. These data show how the DMSO alters the timescales of dissolution, but not the temperature dependence of those timescales. The similarities between activation energies suggest that the co-solvent is not acting to alter the energy barrier to dissolution. Rather, it is providing the ionic liquid with more frequent attempts to infiltrate the cellulose H-bond network and thus only altering the prefactor 'A' in the Arrhenius equation. This result is echoed

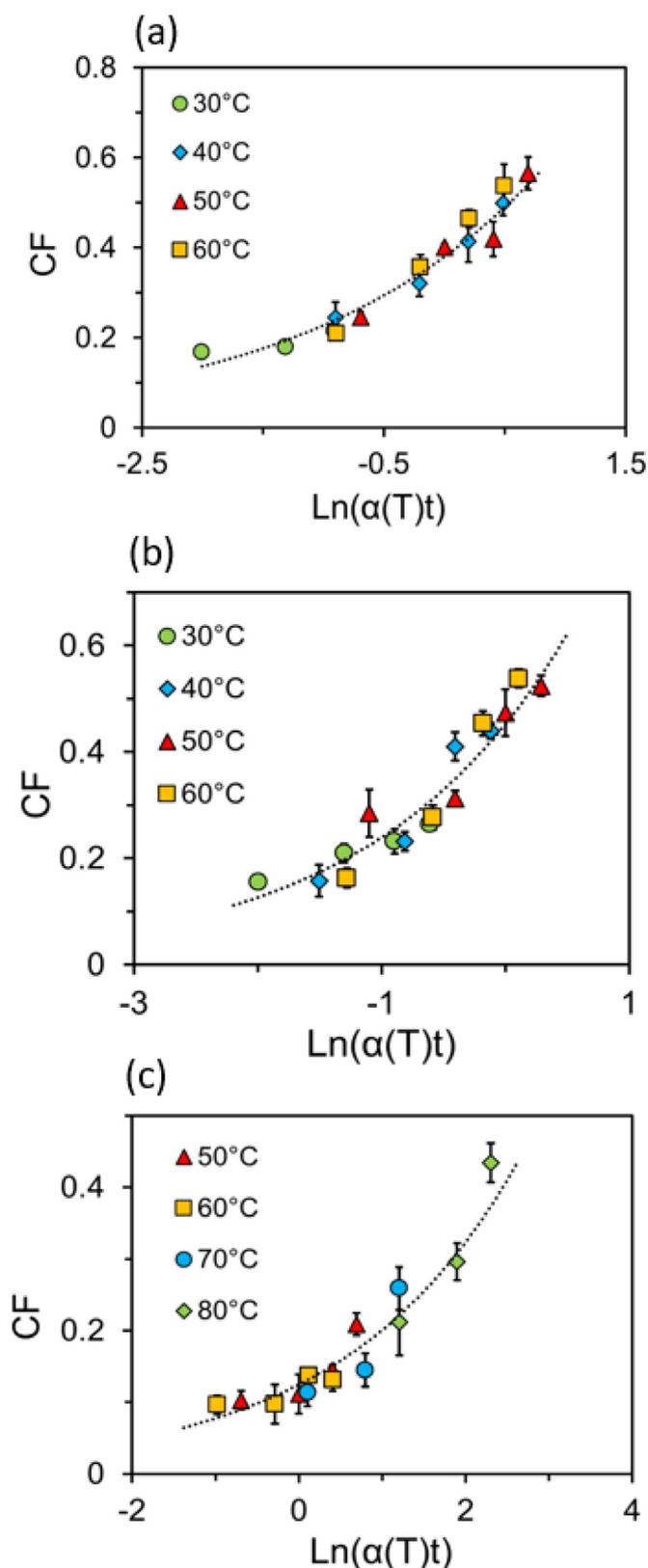


Fig. 6. Master curves of coagulated fraction CF vs  $\ln(\alpha(T)t)$  attained for each concentration of DMSO. a) 20%, b) 50% and c) 75% cosolvent.

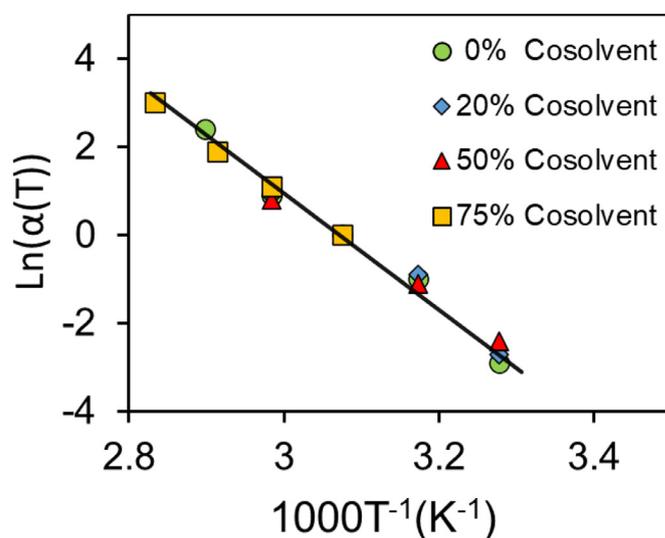


Fig. 7. Arrhenius plot of  $\ln(\alpha(T))$  for each cosolvent concentration and temperature.

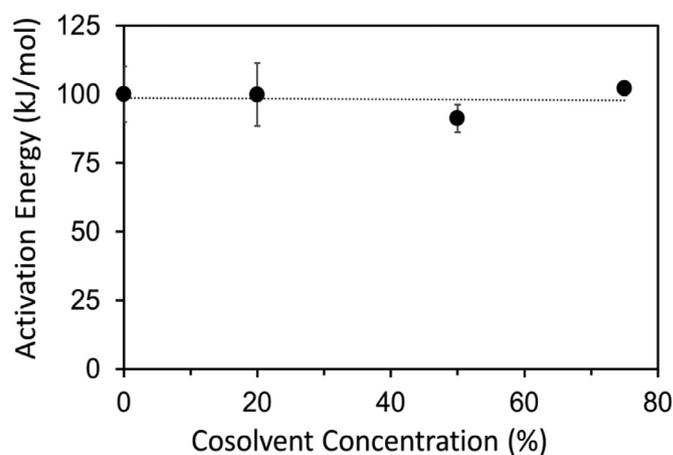


Fig. 8. Activation energy required for cellulose dissolution as a function of cosolvent concentration. A linear fit is used to highlight the consistency of the activation energy.

in the work conducted by Velioglu et al., whereby they conclude that “DMSO has the role of an ‘innocent’ co-solvent, which does not interact strongly with cellulose and does not interfere with the interactions of cellulose with the IL, but lowers the viscosity of the medium, leading to faster mass transport and dissolution” (Velioglu et al., 2014).

The physical notion of an activation energy in a non-solid system is notably more complex than that of a solid system. For a rigid solid, the nature of  $E_a$  is clear- it is the energy barrier that must be overcome for a given molecule to move from its current lattice position to a neighbouring lattice vacancy. When dealing with liquids, or polymer systems however, the picture is not as straightforward. Molecules in such systems are constantly undergoing translational and rotational motion, resulting in ill-defined positions of molecules with a lack of discernible lattice sites. Lingwood et al. report on an appropriate evaluation of  $E_a$  in non-solid systems, stating that  $E_a$  is related to *all* molecular interactions undergone by a molecule as it moves from its initial non-equilibrium state to its final equilibrium state. They denote the timescale on which this happens ‘ $\tau_c$ ’ and claim that  $E_a$  is related to all collisions during this time. Interestingly, in their diffusional study they claim that  $E_a$  does not have a direct relationship with the diffusion coefficient,  $D$ , of the system (Lingwood et al., 2013). Rather,  $E_a$  is more closely related to

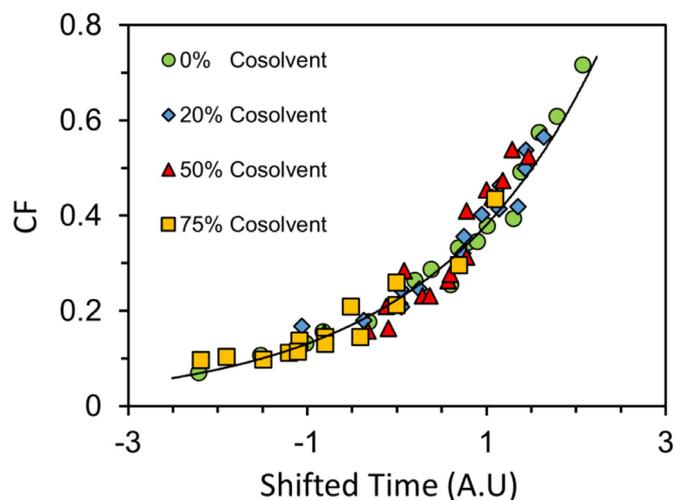


Fig. 9. Master curve showing the coagulation fraction across all temperatures and all cosolvent concentrations.

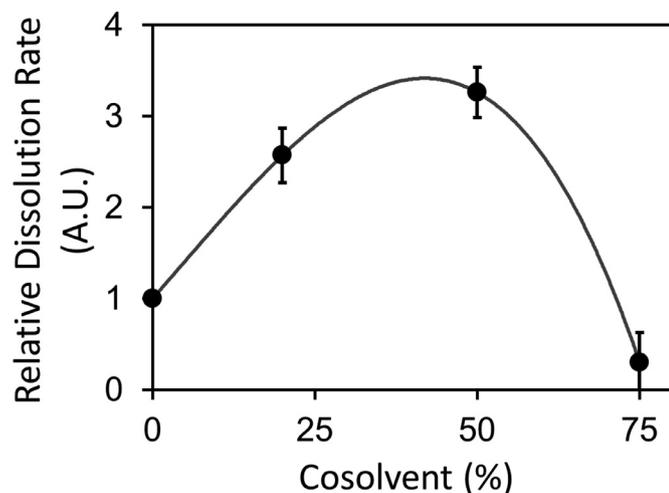


Fig. 10. The relative dissolution speed of flax fibers as a function of cosolvent concentration. Polynomial fit used to guide the eye.

the fluctuation force- which describes the average energetics of all local interactions that occur on the pre-diffusional ( $\sim 1$  ps) timescale.

The cosolvent master curves seen in Fig. 6 can now each be shifted in  $\ln$  time so as to fall onto the same curve for that of the pure ionic liquid results (shown in Fig. 4(d)). The resultant cosolvent master curve, shown in Fig. 9, displays all the results for the CF as a function of time, temperature and cosolvent concentration.

The amounts by which each cosolvent master curve must be shifted in  $\ln$  time to create Fig. 9 act as a direct measure of the relative dissolution rates. For example, the data taken when using a cosolvent concentration of 50% must be scaled by a factor  $\alpha$  of 3.3 in order to overlap with the pure [C2mim][OAc] master curve, hence the dissolution rate is 3.3 times faster at this concentration. Fig. 10 shows how the dissolution rate at each cosolvent concentration varies relative to the dissolution in pure [C2mim][OAc]. Interestingly, the dissolution rate is seen to drop when the concentration of cosolvent is taken above 50% by weight, this corresponds to a DMSO mole fraction of around 0.69. Radhi et al. report that below this concentration, the DMSO preferentially associates with the cation, which may leave many of the anions free to partake in dissolution (Radhi et al., 2015). Above this concentration however, the DMSO couples more favourably with the anion. It is suggested therefore that the drop in dissolving rate of flax fibers at higher DMSO concentra-

tions is not only due to the dilution of the active solvent, but may also be related to the preferential association of DMSO with the anions.

## Conclusions

The dissolution rate of flax fibres in the ionic liquid [C2mim][OAc] has been studied as a function of dissolution temperature and DMSO cosolvent concentration. Fig. 1 shows that during dissolution, a layer of coagulated cellulose forms around the fibrous core and the two regions are noticeably different in their appearance when viewed under an optical microscope. This difference, highlighted in Fig. 2, allowed for the quantification of the amount of coagulated cellulose as a function of both dissolution time and temperature. The formation of coagulated material slows at longer times and the slowing is thought to be due to the outer layer acting as a barrier between solvent and fibre. Upon changing the dissolution temperature, the timescales on which the coagulated material forms were altered, with higher temperatures resulting in a more rapid rate of growth, shown clearly in Fig. 3. This finding suggested an equivalence between time and temperature, which was subsequently verified by the shifting of data in the natural logarithmic time domain. When shifted, each temperature dependant data set was found to overlap, forming a master curve.

The shift factors used to generate this master curve were plot against the inverse of their respective temperatures. Upon doing so, a linear relation revealed Arrhenius behaviour in the system. As a result, an activation energy was calculated- describing the energy required for the dissolution of flax fibres in [C2mim][OAc]. This energy was found to be  $100 \pm 10$  kJ/mol.

The cosolvent DMSO was found to modify the rate of dissolution of flax fibres, though the temperature dependence of the timescales of dissolution remained remarkably constant. The activation energy of dissolution for each DMSO concentration is shown in Fig. 8 to be very consistent, with all values falling within the range  $100 \pm 10$  kJ/mol.

Fig. 10 shows the relative dissolution speed as a function of cosolvent concentration. The dissolution rate is seen to be maximised when using an equal amount of ionic liquid to cosolvent, whereby the dissolution process occurs 3.3 times faster than dissolution in pure [C2mim][OAc].

The independence of  $E_a$  on DMSO concentration strongly suggests that the dissolution of flax fibres is not purely a viscosity driven process. This result mirrors the recent findings of Chen et. al, whereby it is noted that the dissolution (of cellulose fibres) is not governed primarily by viscosity, but instead by solvent power (Chen et al., 2020a).

Finally, the work undertaken here may be of interest to the growing study of all cellulose composites (Nishino et al., 2004; Gindl & Keckes, 2005) The preparation of all cellulose composites with good mechanical properties requires the controlled partial dissolution of the cellulosic fibres for optimum bonding, without significant loss of the fibre mechanical properties (Chen et al., 2020b). The results presented here will assist in the optimisation of future cellulose based composites, through quantitative control of the dissolution using time, temperature and cosolvent concentration .

## Declaration of Competing Interest

None.

## Acknowledgements

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All data can be found at: <https://doi.org/10.5518/877>

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.carpta.2020.100021.

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