Aalto University
School of Chemical
Engineering

Dissolution of cellulose

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CHEM-E2140 Cellulose-based fibres

Learning objectives

After this lecture, the student should be able to:

- Distinguish the thermodynamics of polymer dissolution from dissolution of small molecular components
- List the most common cellulose solvents
- Describe how the most common cellulose solvents work
- Be aware of the specific limitations of the most common cellulose solvents

Contents outline

(1) Background:
- Why to dissolve cellulose?
- Challenges in cellulose dissolution
- Basic concepts

(2) Generic treatise on polymer dissolution and swelling of cellulose

(3) Properties of some cellulose solvents

(4) Properties of widely used, important modern solvents:
- Dimethylacetamide / LiCl
- Urea / NaOH / water
- N-methylmorpholine N-oxide (NMMO) / water
- Ionic liquids

Motivation: Why dissolve cellulose?

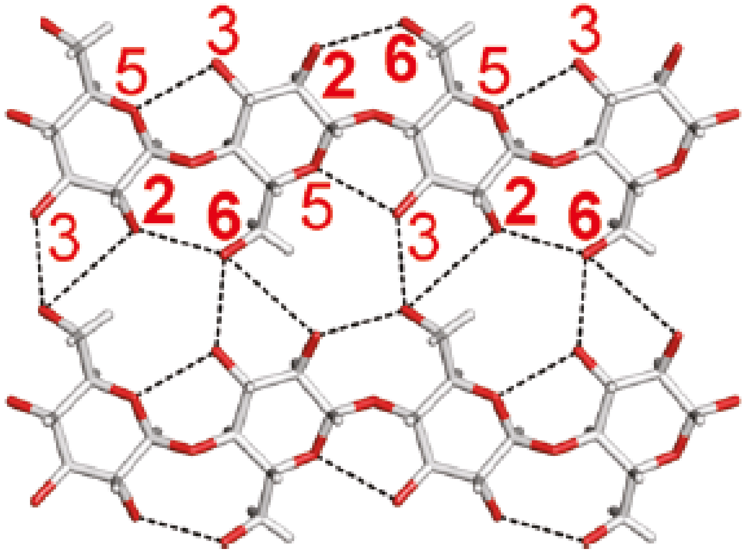
- To prepare regenerated cellulose from dissolved cellulose
    - fibres (e.g., cellulose II is suitable for textiles)
    - films (e.g., packaging purposes)

- To chemically modify cellulose in a *homogeneous* environment
    - Most solvents cannot penetrate inside crystalline cellulose

    → heterogeneous modification is restricted only to the surface of crystalline cellulose

- To degrade cellulose more efficiently
    - Cellulose is degraded much more efficiently in a homogeneous environment than in a heterogeneous one

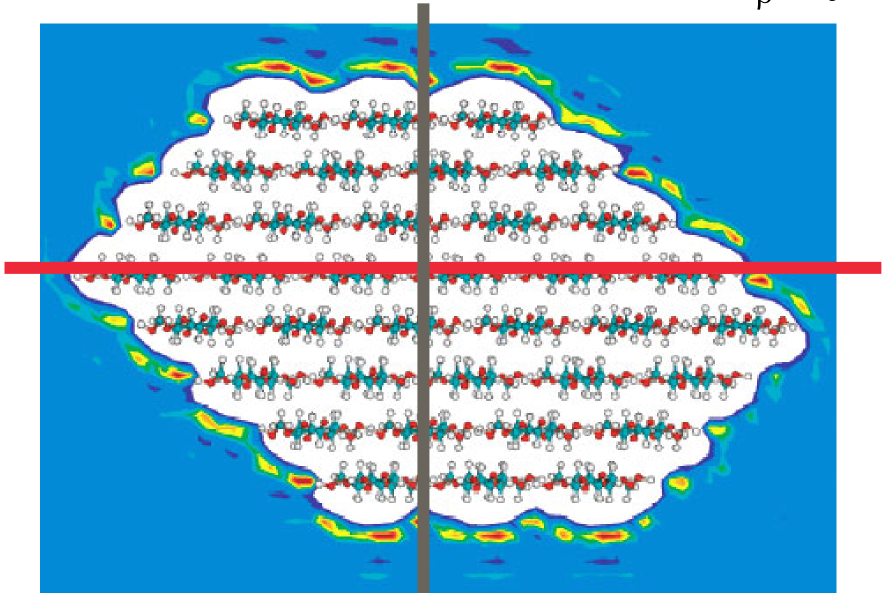
Cellulose dissolution: challenges



The hydrogen bonding network in crystalline cellulose is exceptionally strong.

Cellulose dissolution: challenges

Radial cross section of a cellulose I$_\beta$ crystallite:



Cellulose **crystal** is exceptionally recalcitrant to dissolution.

Within the sheets:
hydrogen bonds

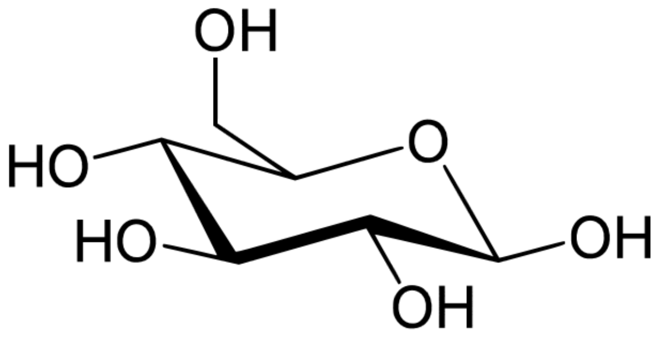
Between the sheets:
van der Waals bonds

Cross sectional image taken from: Gross and Chu *J. Phys. Chem. B* **2010**, *114*, 13333.

Cellulose dissolution: challenges

NOTE: Hydrogen bonding does not automatically imply difficult solubility

- Most hydrogen bonded substances dissolve in water because H-bonding between water and the compound is stronger than between the compound molecules themselves

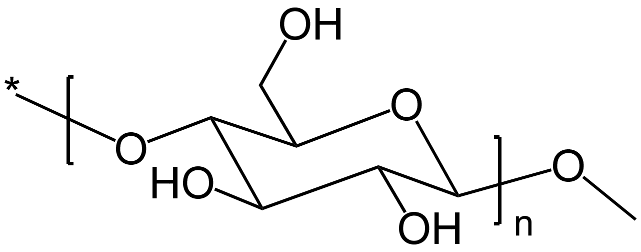


FOR EXAMPLE:
Glucose dissolves in water although it is hydrogen bonded and crystalline in solid state.

NOTE: Crystallinity itself does not imply difficult solubility

- Many crystalline systems dissolve in water
- In case of cellulose, also amorphous cellulose is insoluble in common solvents

Cellulose dissolution: challenges



- Cellulose is amphiphilic: it contains both hydrophlic and hydrophobic sites

Interesting recent account on amphiphilicity and insolubility of cellulose:
Medronho et al. *Cellulose* **2012**, *19*, 581.

Cellulose dissolution: basic concepts

Derivatizing solvent: ← **Note: not really a solvent**

- A solvent which induces covalent modifications on the cellulose backbone
- The modification must be easily removable

Non-derivatizing solvent:

- A solvent which truly separates the individual cellulose chains from each other without chemical modification

Here, we will deal exclusively with non-derivatizing solvents.

Cellulose dissolution: basic concepts

Tricomponent solvents

- For example, NH_3/SO_2/DMSO

Bicomponent solvents

- For example, dimethylacetamide/LiCl, NMMO/H_2O, Cu/ethylenediamine

Unicomponent solvents

- Ionic liquids

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Generic treatise on polymer dissolution and swelling of cellulose

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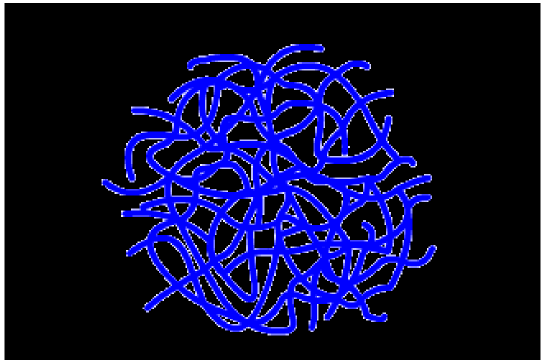
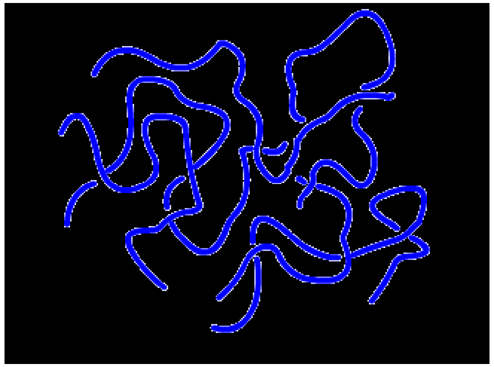
Dissolution of polymers in general

Polymers do not dissolve like small molecular compounds

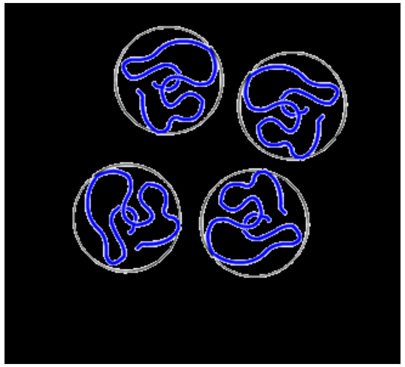
(1) First, the solvent swells them
(2) If the dissolving power is great enough, individual chains separate from each other, causing a dissolved state



Solid state



Swelling



Dissolution

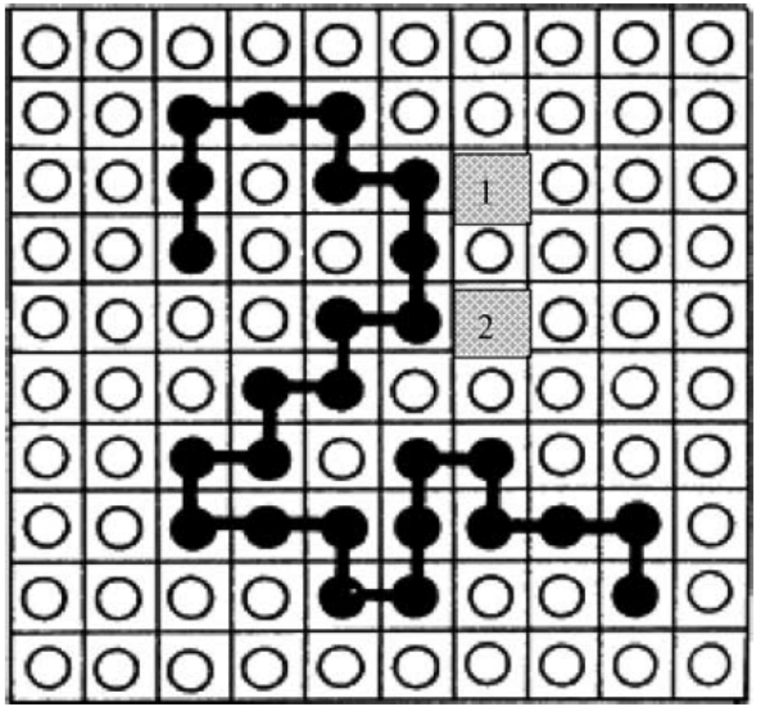
Dissolution of polymers in general

Second law of thermodynamics:
$\Delta G = \Delta H - T\Delta S$

In dissolution:
ΔG – Gibbs free energy
ΔH – enthalpy of mixing
T – absolute temperature
ΔS – entropy of mixing

- ΔG must be negative for dissolution to occur
- Positive $\Delta H \rightarrow$ polymer and solution are at their lower energy state
- Negative $\Delta H \rightarrow$ polymer solution is at its lower energy state

Dissolution of polymers in general

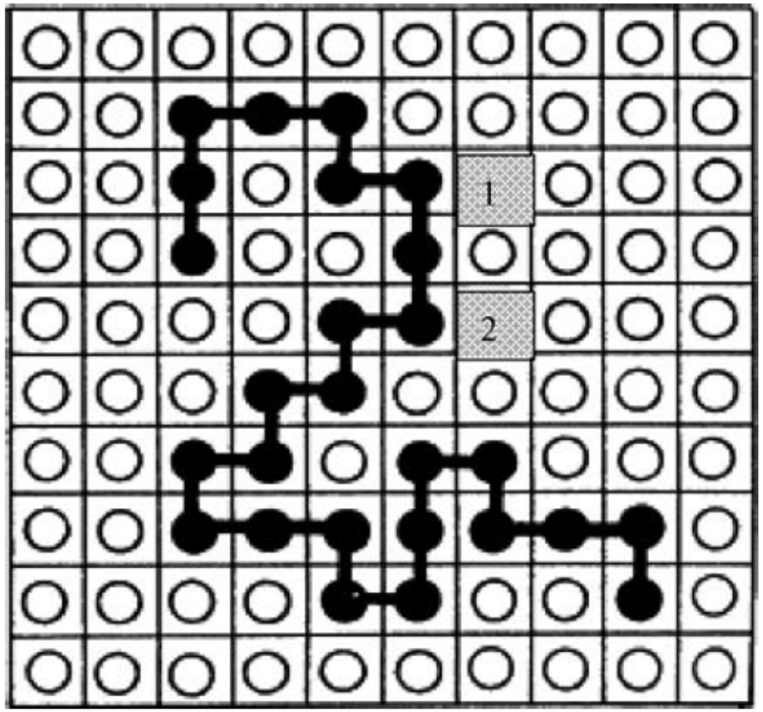


Configurational entropy of mixing (Boltzmann equation):

$\Delta S = k \ln W$

where k is the Boltzmann constant and W is the number of possible arrangements within the lattice

Dissolution of polymers in general

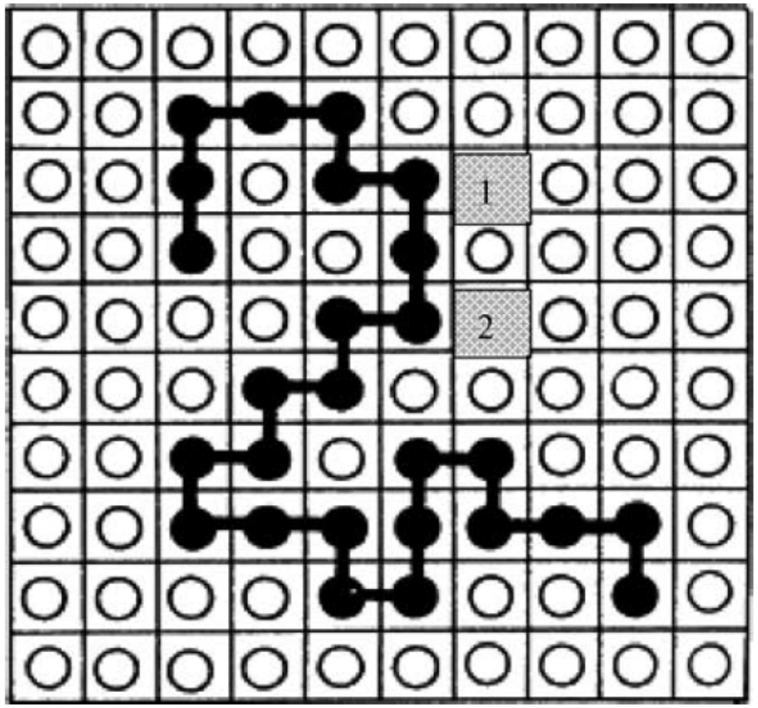


If segments 1 and 2 are connected (as they are in a polymer)

→ ΔS = k lnW is immensely smaller than with small molecular compounds which are not connected to each other

Flory *J. Chem. Phys.* **1942**, *10*, 51.
Huggins *J. Phys. Chem.* **1942**, *46*, 151.

Dissolution of polymers in general



$$\Delta S_m = -k[n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

$$\phi_1 = \frac{n_1}{n_1 + n_2 x} = \frac{N_1}{N_1 + N_2 x},$$

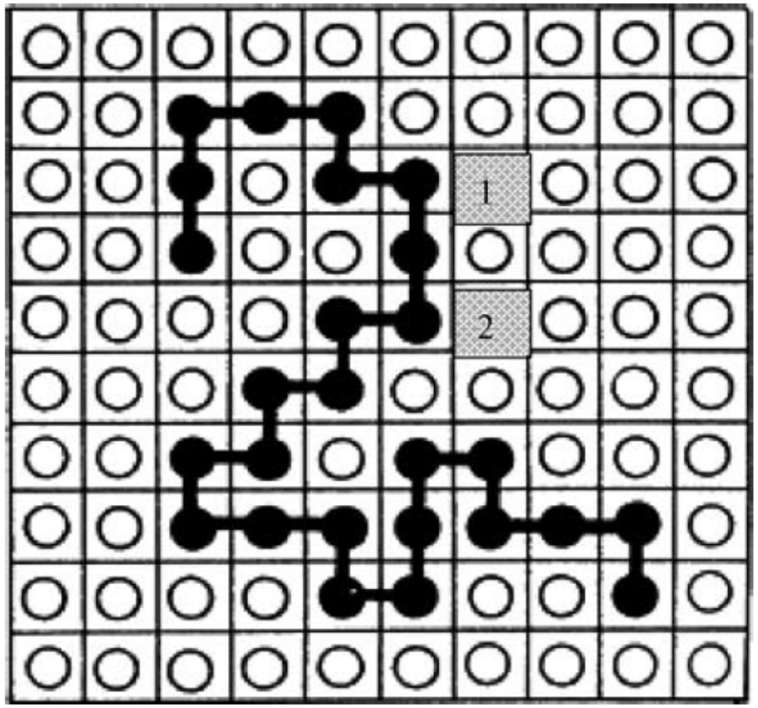
$$\phi_2 = \frac{n_2 x}{n_1 + n_2 x} = \boxed{\frac{N_2 x}{N_1 + N_2 x}}$$

where
n - the number of molecules
N - the mole fraction
x - the degree of polymerization
(**Subscripts 1: solvent, 2: polymer**)

→ Volume fraction (ϕ_2) increases with x
→ Entropy of mixing is large and is the dominant factor in dissolution

Flory *J. Chem. Phys.* **1942**, *10*, 51.
Huggins *J. Phys. Chem.* **1942**, *46*, 151.

Dissolution of polymers in general



Entropy of *dilution* or the chemical potential of the solvent ($\Delta\mu_1$) is considered. This is related to osmotic pressure (π):

$$\pi = -\left(\frac{RT}{V_1}\right)\left[\ln(1-\phi_2) + \left(1-\frac{1}{x}\right)\phi_2 + \chi\phi_2{}^2\right]$$

where V is the mole volume and χ is the interaction parameter
→ $\chi < 0.5$ → polymer dissolves

Flory *J. Chem. Phys.* **1942**, *10*, 51.
Huggins *J. Phys. Chem.* **1942**, *46*, 151.

Dissolution of polymers in general

NOTE 1: The Flory-Huggins theory does not take into account the accessibility of monomeric units by the solvent.

NOTE 2: The Flory-Huggins theory does not take into account the hydrophobic interactions in aqueous systems (common with biological macromolecules).

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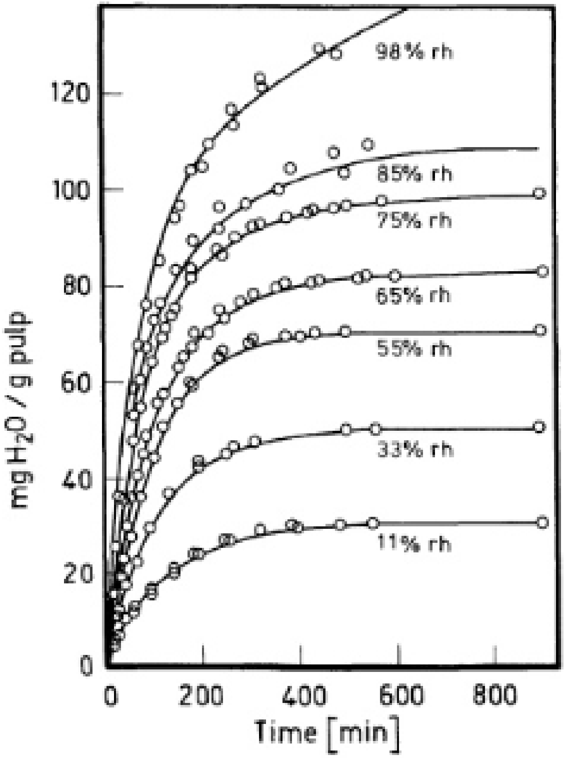
Swelling of cellulose

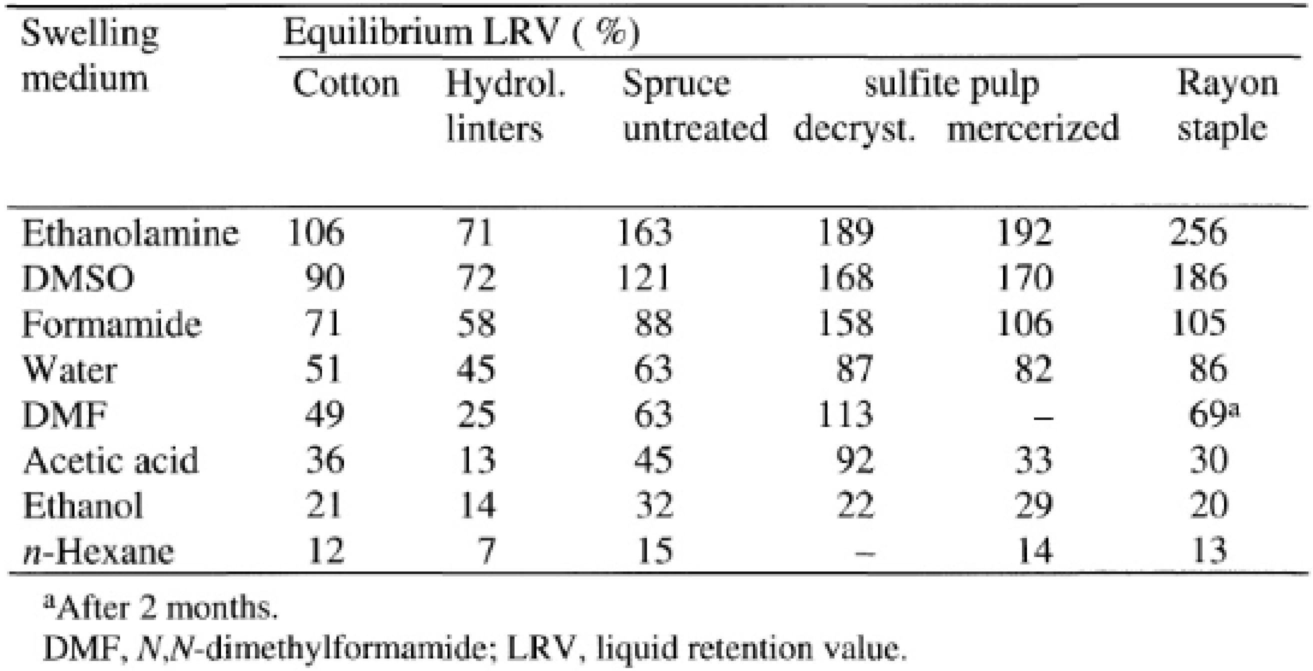


- Cellulosic substrates (usually fibres) swell extensively in many polar solvents, notably in water
- Left, water vapour sorption of spruce sulfite pulp at different relative humidities

Philipp *Ph.D. Thesis* **1952**.

Swelling of cellulose

Swelling of cellulosic fibres in some common organic solvents (and water)



Swelling medium	Equilibrium LRV (%)					
	Cotton	Hydrol. linters	Spruce untreated	sulfite pulp decryst.	mercerized	Rayon staple
Ethanolamine	106	71	163	189	192	256
DMSO	90	72	121	168	170	186
Formamide	71	58	88	158	106	105
Water	51	45	63	87	82	86
DMF	49	25	63	113	–	69[a]
Acetic acid	36	13	45	92	33	30
Ethanol	21	14	32	22	29	20
n-Hexane	12	7	15	–	14	13

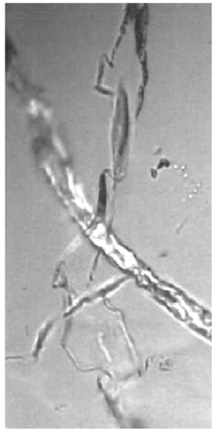
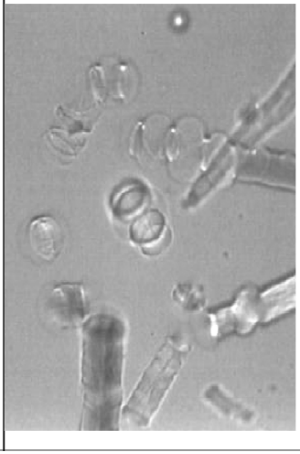
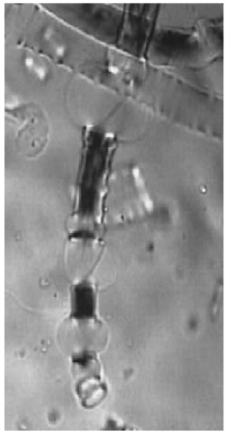
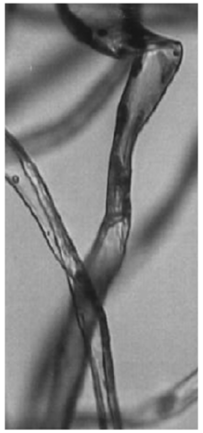
[a] After 2 months.

DMF, *N*,*N*-dimethylformamide; LRV, liquid retention value.

Many common solvents are good swelling agents for cellulose but *none* of them manage to dissolve cellulose.

Klemm et al. *Comprehensive Cellulose Chemistry Vol. 1*
Wiley-VCH, 1998, p.52.

General considerations on cellulose swelling prior to dissolution

Content of water	< 17%	19 – 24%	25 – 35%	> 35%
Swelling and dissolution mechanism	Dissolution by disintegration in spindle (Mode 1)	Swelling by ballooning, dissolution (Mode 2)	Swelling by ballooning, no dissolution (Mode 3)	Homogeneous swelling, no dissolution (Mode 4)
10 μm ●–●	Wood fibre 	Wood fibre 	Wood fibre 	Cotton fibre 

Cuissinat and Navard *Macromol. Symp.* **2006**, *244*, 1.

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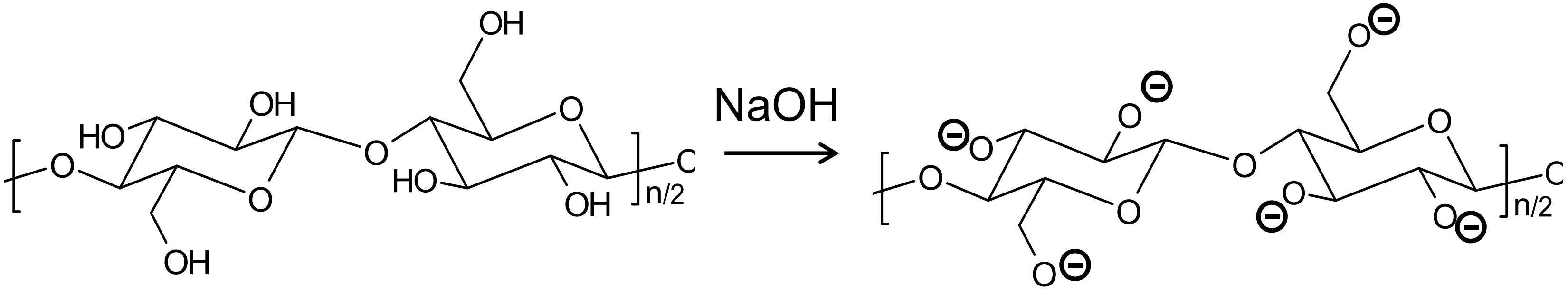
Traditional cellulose solvents:

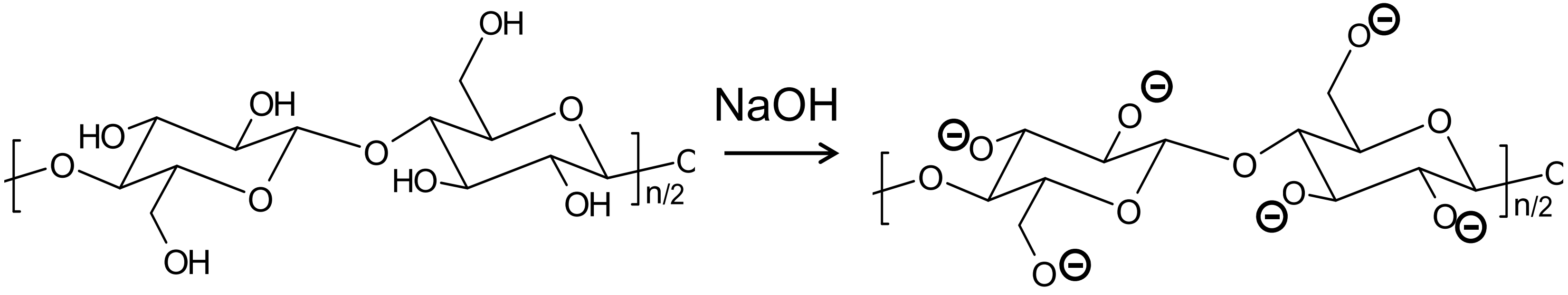
NaOH / water
Phosphoric acid / water
Transition metal complexes

NaOH / water



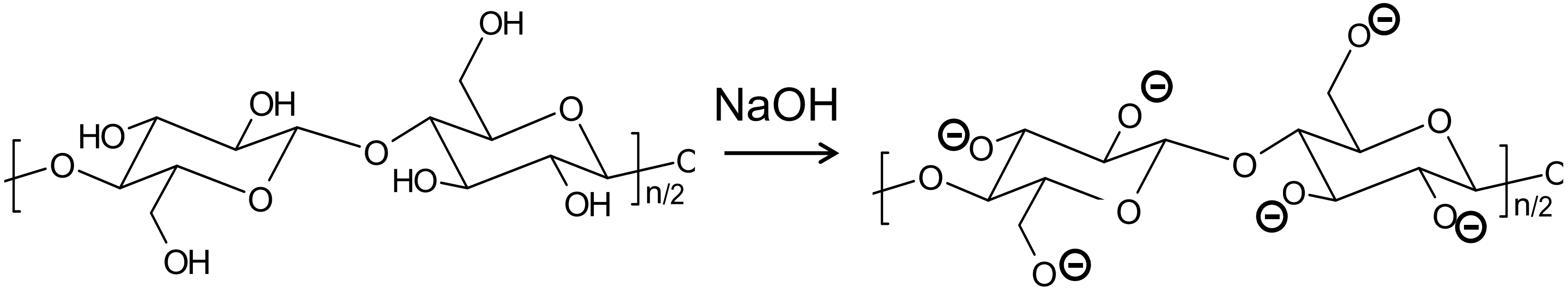
- At strong NaOH concentrations (5-35%), the hydroxyl groups are dissociated
- Dissolution usually requires a freeze/thaw pretreatment and/or subzero temperature (e.g., -6°C) during dissolution

NaOH / water



- Several semi-crystalline cellulose grades dissolve in 5-20% NaOH after proper pretreatments
- Some grades (e.g., native cotton) have limited solubility
- Amorphous cellulose has been shown to dissolve in 4% NaOH

NaOH / water



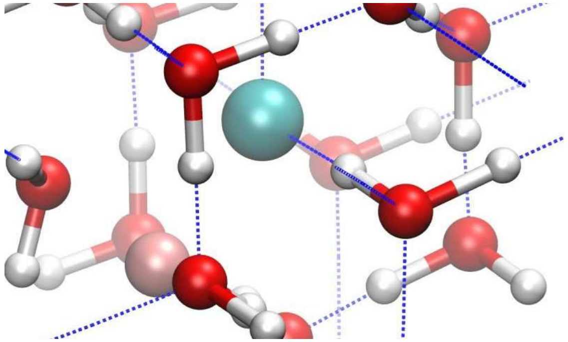
- Chain degradation due to alkaline hydrolysis occurs upon dissolution
- OH-group dissociation does not fully explain cellulose dissolution in NaOH

Hermans and Weidinger *JACS* **1946**, *68*, 2547.
Isogai *Cellulose* **1997**, *4*, 99.

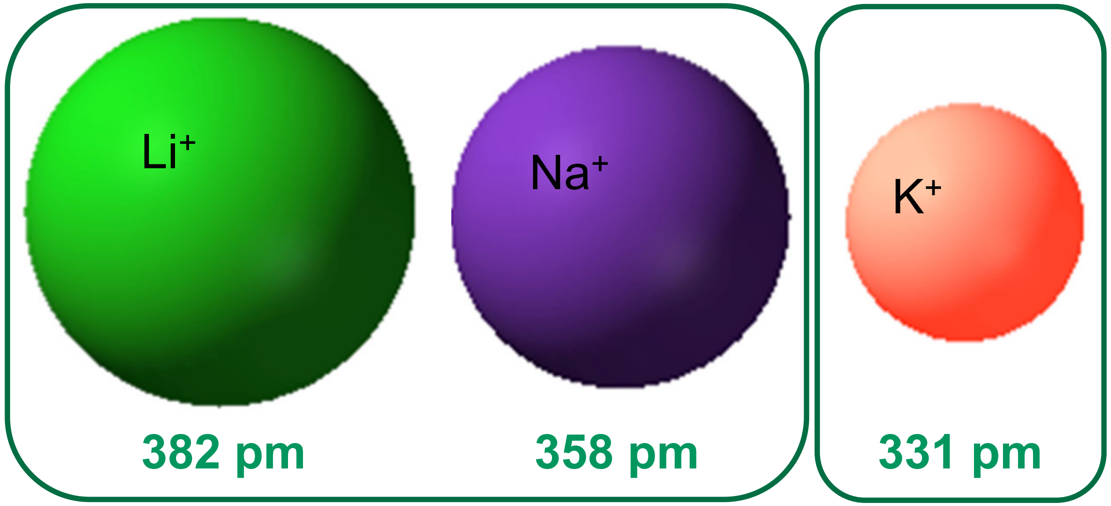
Isogai and Atalla *Cellulose* **1998**, *5*, 309.
Le Moigne and Navard *Cellulose* **2010**, *17*, 31.

NaOH / water – dissolution mechanism

Ions are hydrated in water



Radius of hydration (binding of water molecules) is in the order $Li^+ > Na^+ > K^+$



LiOH and NaOH dissolve cellulose

KOH does not dissolve cellulose

- OH^- breaks cellulose hydrogen bonds
- Na^+ (or Li^+) stabilises the anoinic cellulose-OH^- complex

Xiong et al. *Cellulose* **2013**, *20*, 613.

Phosphoric acid / water

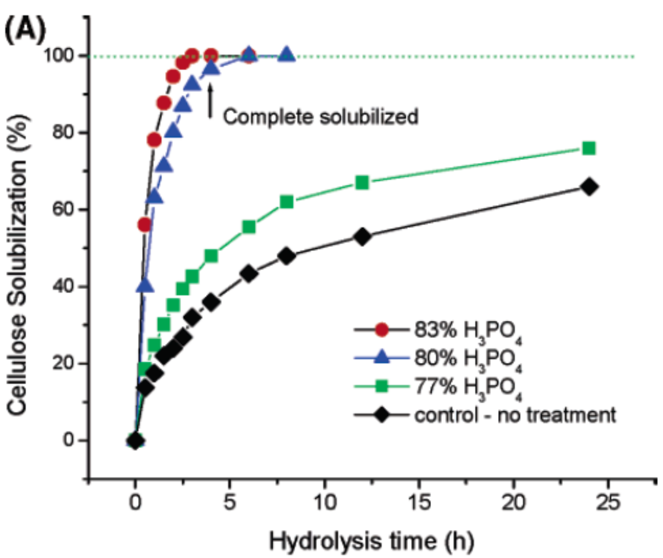
- Concentrated phosphoric acid (~80%) is a considerable swelling agent for cellulose

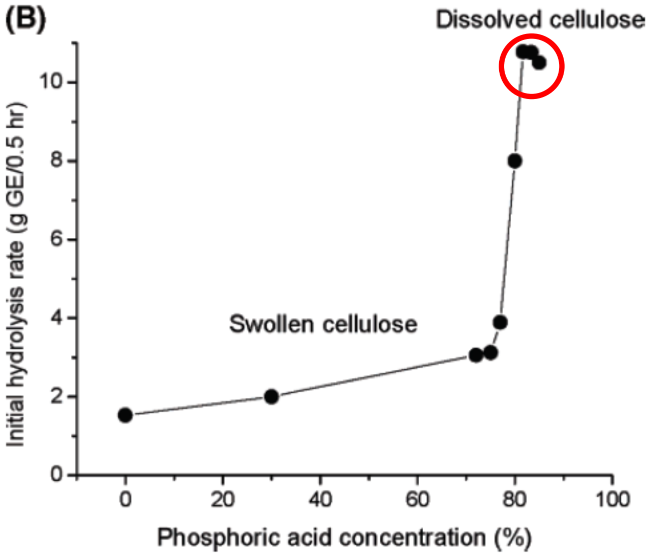
- Swelling in phosphoric acid changes the crystallinity: from crystalline to amorphous (Walseth *Tappi* **1952**, *35*, 228)

- Phosphoric acid swollen cellulose (PASC) is used to assess the activity of cellulose degrading enzymes (cellulases) because of its high accessibility

Phosphoric acid / water

Enzymatic hydrolysis of phosphoric acid swollen cellulose:

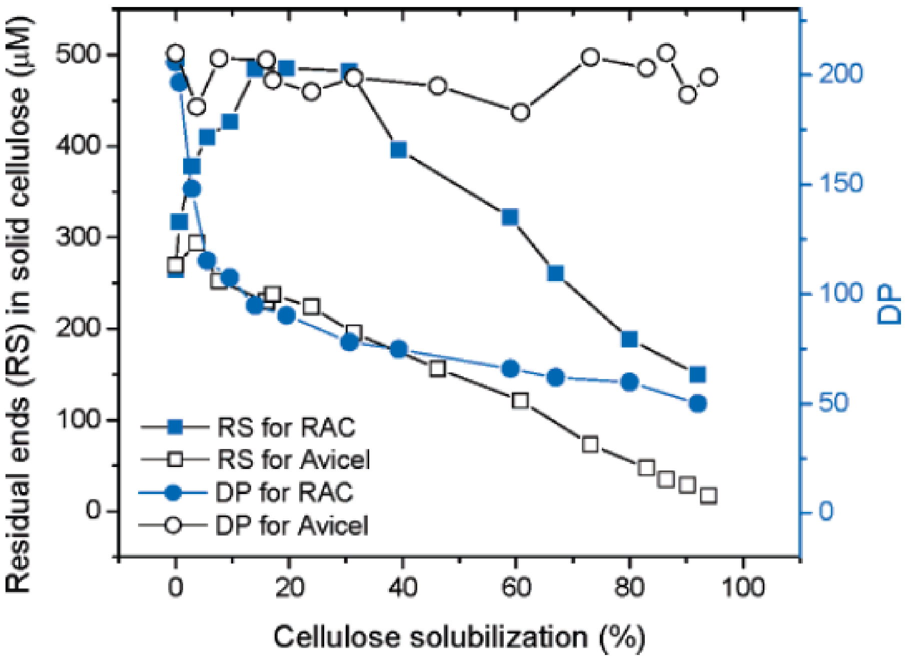




- At ca. 83% H_3PO_4 concentration, cellulose dissolves completely

Zhang et al. *Biomacromolecules* **2006**, *7*, 644.

Phosphoric acid / water



- Considerable chain degradation during dissolution
- Minor formation of phosphate esters during dissolution

RAC – regenerated amorphous cellulose
Acivel – hydrolyzed cellulose I grade with high crystallinity

Zhang et al. *Biomacromolecules* **2006**, *7*, 644.

Transition metal complexes

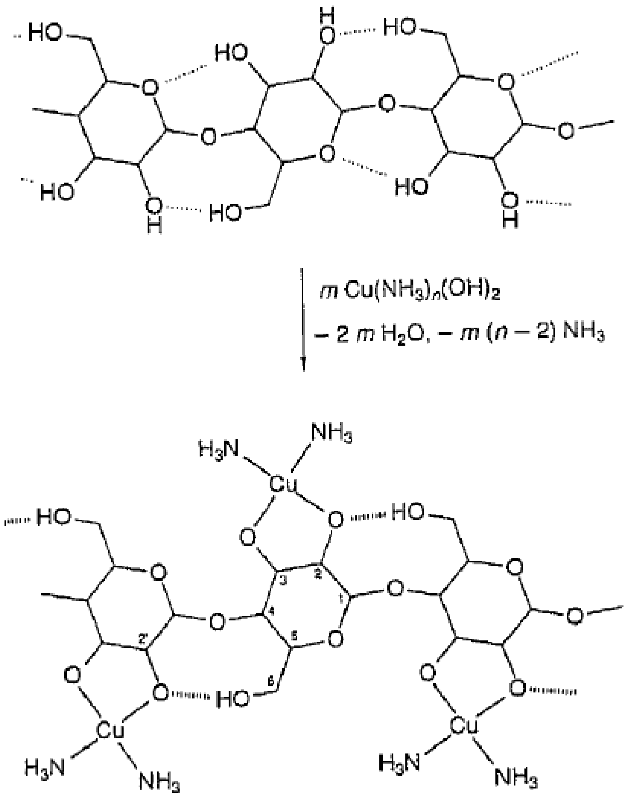
Transition metal complexes that dissolve cellulose include:

- Copper complex with ammonia (Cuoxam): first known solvent for cellulose (1857)
- Copper complex with ethylenediamine (Cuen): still used for simple molecular weight determination of cellulose by viscometry

- Cadmium complex with ethylenediamine (Cadoxen)
- Ferric tartraic acid complex in alkaline solution (FeTNa)

Aside the viscosity determination by Cuen, these solvents are not very popular at present.

Cuoxam



- Aqueous ammonia solution of copper(II) hydroxide
- Also known as *Schweizer's reagent*

- Hydroxyl groups of cellulose are deprotonated (OH→O^-) in the presence of Cu(II) ions and form chelate complexes

Burchard et al. *Angew. Chem. Int. Ed.* **1994**, *33*, 884.

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Widely used modern solvents

Dimethylacetamide / LiCl
NaOH / urea / water
N-methylmorpholine oxide (NMMO) / water
Ionic liquids

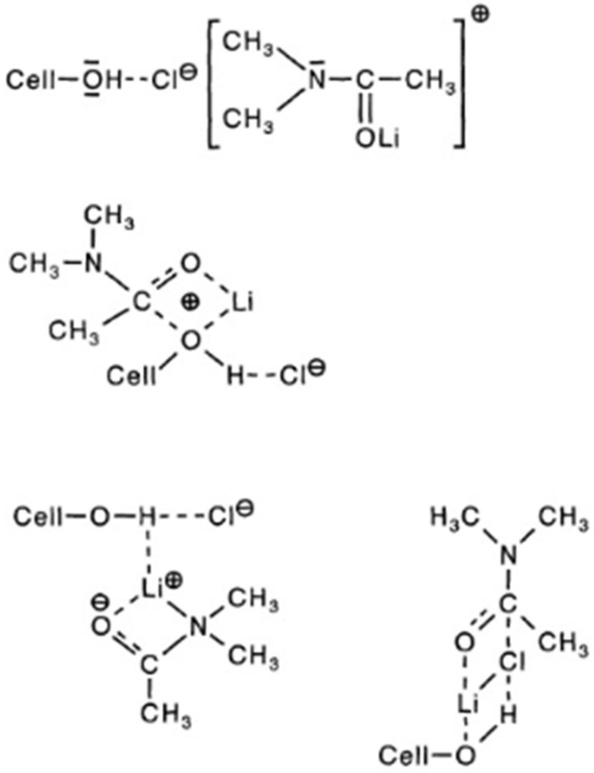
Dimethylacetamide / LiCl

- The most common laboratory solvent for cellulose
- Generally, 8.47 w% LiCl in DMAc is used (saturation concentration); the dissolution requires activation by solvent exchange
- Effortless and reliable: negligible chain degradation of cellulose within the span of several months

Used for:

- Laboratory-scale chemical modification of cellulose in homogeneous environment
- Measuring the molecular weight distribution of cellulose with gel permeation chromatography (GPC)
- Quantification of carbonyl (C=O) groups in cellulose by fluorescent labelling

Dimethylacetamide / LiCl



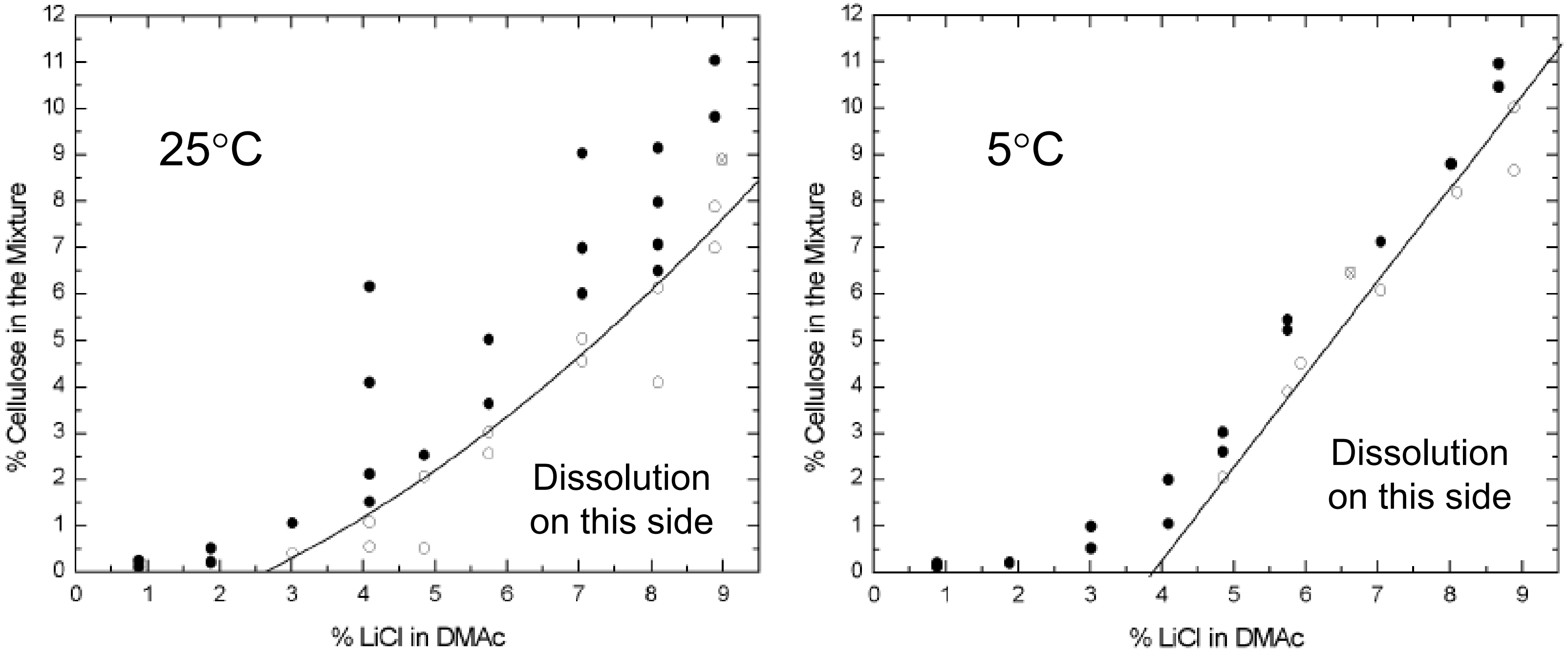
- Dissolution mechanism is based on hydrogen bond complexation in cellulose by DMAc/LiCl complex

Dawsey and McCormick
J. Macromol. Sci – Rev. Macromol. Chem. Phys. **1990**, *C30*, 405.

Dimethylacetamide / LiCl

Phase diagrams of LiCl/DMAc/Cellulose

Note: a notable effect in LiCl concentration!



● Biphasic samples (incl. non-dissolved cellulose or liquid crystals)

○ Isotropic points

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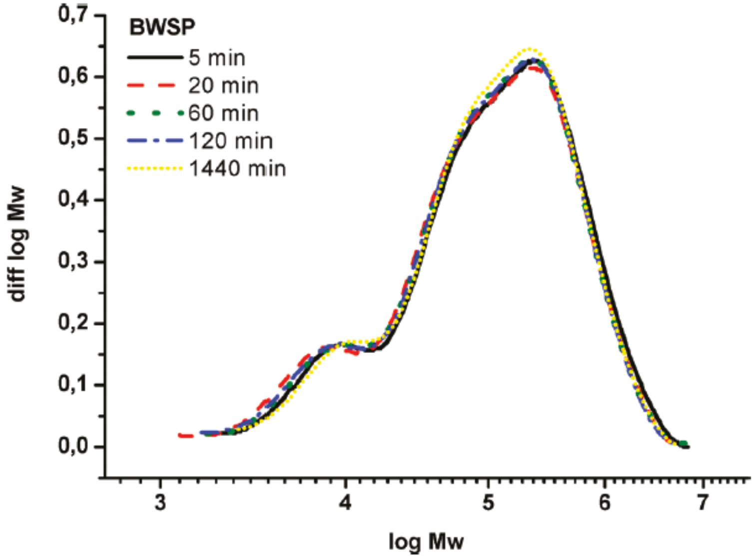
Chrapava et al. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1842.

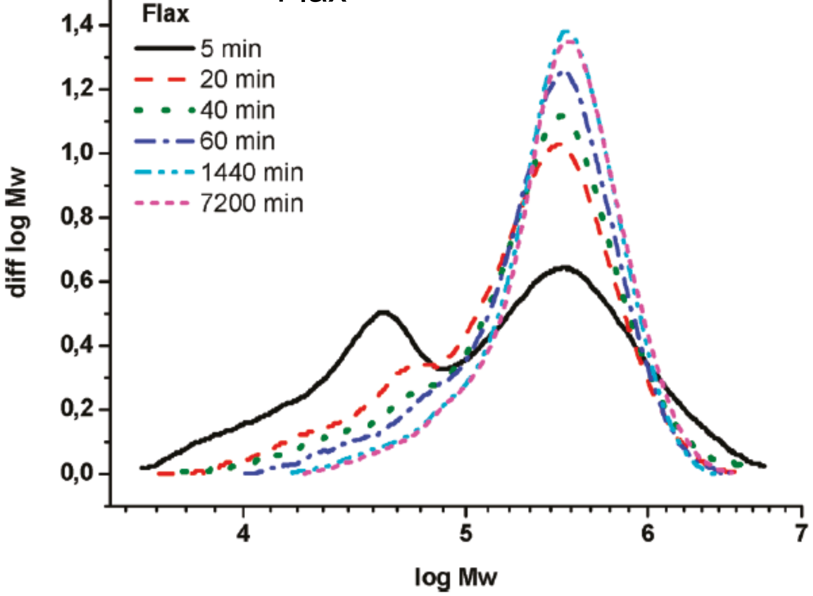
Dimethylacetamide / LiCl

Time dependency of dissolution time of cellulose from different plant fibres
Gel permeation chromatograms:

Bleached beached sulphite pulp



Flax



→ Annual/perennial plants take longer to dissolve than wood-based fibres

Henniges et al. *Biomacromolecules* **2011**, *12*, 871.

Dimethylacetamide / LiCl – practical aspects

Preparation of the solvent (DMAc/LiCl)

- heat DMAc into ~100°C
- add 8.47% (w/w) LiCl (saturation concentration)
- filtration

Dissolution in practice:

(1) Solvent exchange:
  - 3×methanol
  - 2×dimethylacetamide

(2) Slow addition of solvent exchanged cellulose in DMAc/LiCl

(3) Dissolution for at least overnight before the solution is ready to use

Dimethylacetamide / LiCl – practical aspects

(1) The water content of the used DMAc should be below 0.9 wt%

(2) Sufficient time of dissolution (overnight) is necessary

(3) The higher the LiCl amount, the longer the possible storage time before aggregation sets in

Röder et al. *Macromol. Symp.* **2002**, *190*, 151.

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Urea / NaOH / water

- Among the most recently introduced cellulose solvents (Introduced in 2000 by Lina Zhang)

- Dissolution with 7 wt% NaOH and 12 wt% urea at -12°C

- Solvent is particularly used for preparation of “high-end” cellulose materials:
    - photoluminescent films
    - fluorescent cellulose hydrogels with quantum dots
    - superabsorbent hydrogels with controlled delivery
    - Fe_3O_4/cellulose microspheres with magnetic-induced protein delivery

  etc.

Urea / NaOH / water

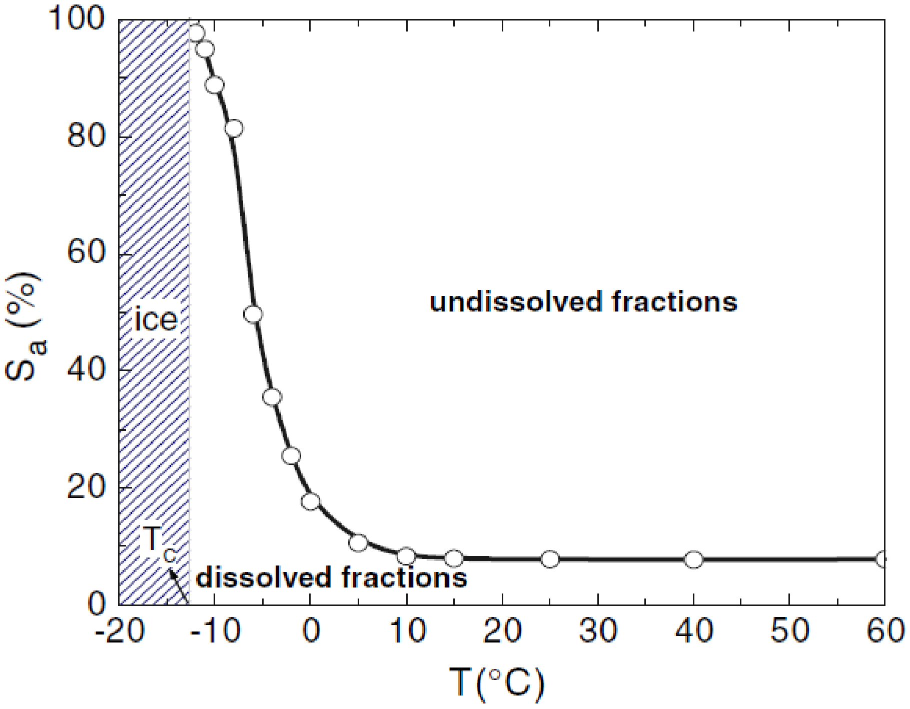
Mechanism:

- Hydrogen bonding networks of urea/NaOH/water clusters form new hydrogen bonding networks at low temperatures
- Cellulose forms wormlike inclusion complexes with these clusters
- Quick dissolution is attributed to dynamic self-assembly leading to the inclusion complex

NOTE: Urea / NaOH / water is probably the fastest solvent for cellulose with dissolution occurring in less than 2 minutes.

Urea / NaOH / water

Temperature dependence



$$S_a = (W_0 - W_i)/W_0 \qquad (1)$$

where W_0 is weight of original cellulose, and W_i is weight of the undissolved fractions.

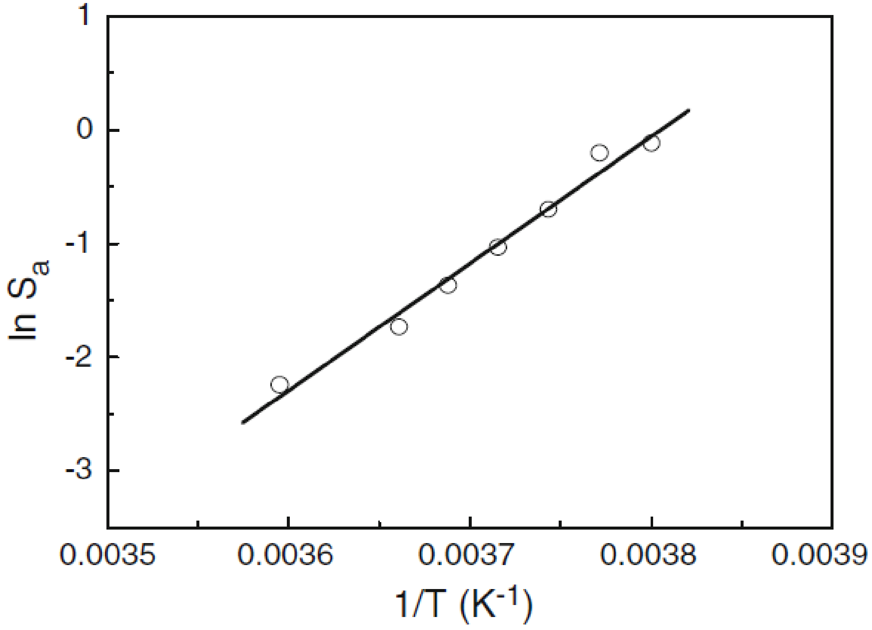
Note: -12.6°C is the critical point for the solvent

Qi et al. *Cellulose* **2008**, *15*, 779.

Urea / NaOH / water

Temperature dependence

Arrhenius plot



Activation energy of dissolution ($E_{a,s}$) from Arrhenius equation:

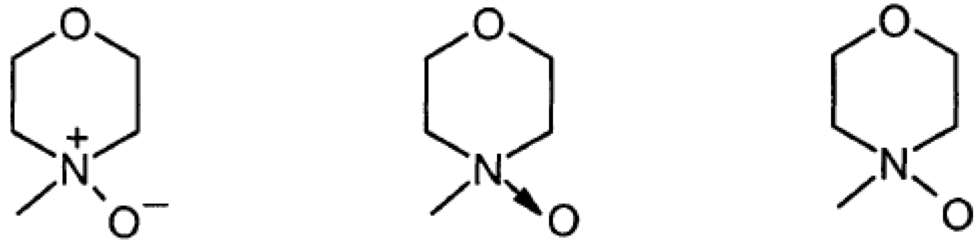
$$\ln S_a = \ln A - E_{a,s}/RT$$

→ $E_{a,s}$= -101 kJ/mol

→ Negative enthalpy implies that cellulose dissolution with urea/NaOH/water is an entropy-driven process

NMMO

3 possible formulae of *N*-methylmorpholine-*N*-oxide

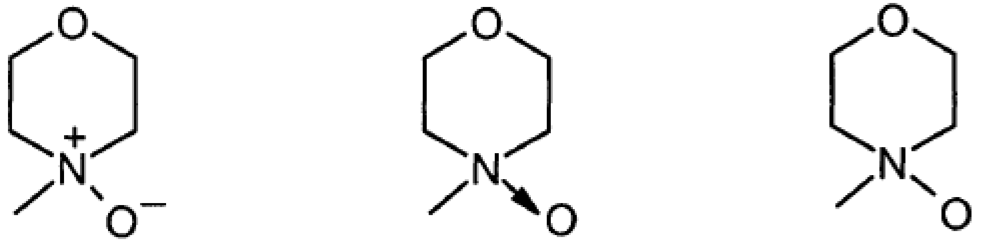


Predominant feature of NMMO is the highly dipolar N-O bond

- The only industrial solvent for cellulose regeneration
- Introduced in early 1980s (Chanzy, *J. Polym. Sci.* **1982**, *20*, 1909)
- Used in the Lyocell process

NMMO

3 possible formulae of *N*-methylmorpholine-*N*-oxide



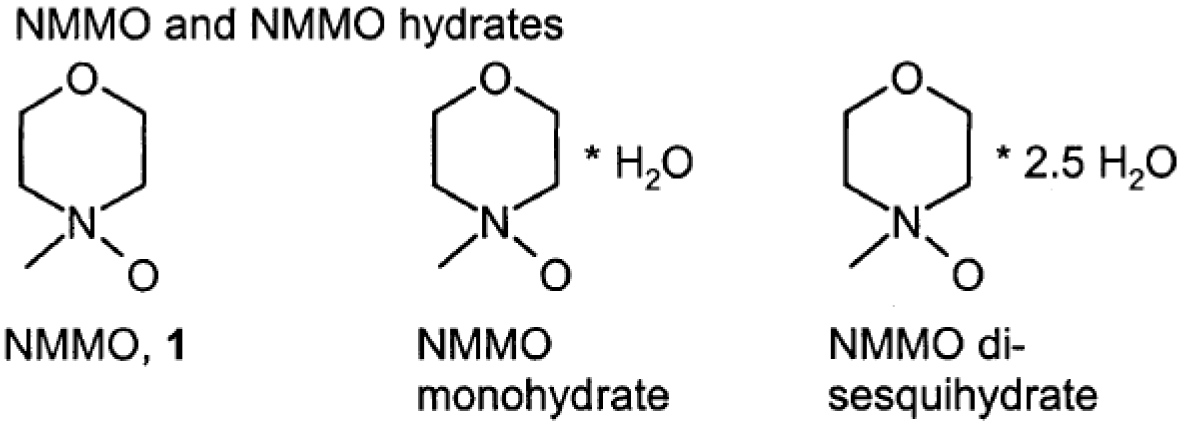
Predominant feature of NMMO is the highly dipolar N-O bond

Properties of NMMO:

- Pronounced tendency to form hydrogen bonds
- Strong oxidant (N-O bond is easily broken)
- Slightly basic (pK_b=9.25)
- Thermally labile

NMMO

Hydrate formation with water


NMMO and NMMO hydrates

NMMO, 1

NMMO monohydrate

NMMO di-sesquihydrate

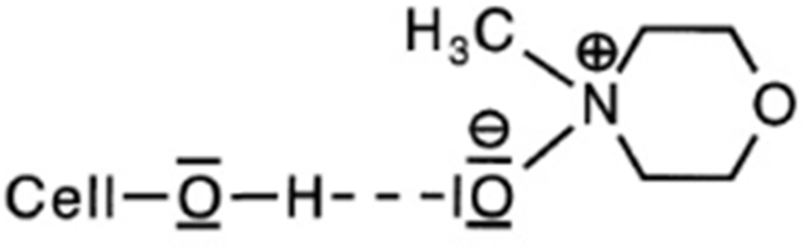
13.3% (w/w) water

28% (w/w) water

- The N-O bond is able to form 1 or two hydrogen bonds with two partners containing hydroxyl groups (e.g., water or cellulose)
- Cellulose dissolution occurs generally between 4-17% water content
- When the water content exceeds monohydrate concentration, the ability to cellulose severely decreases (no hydrogen bonding ability left)

NMMO

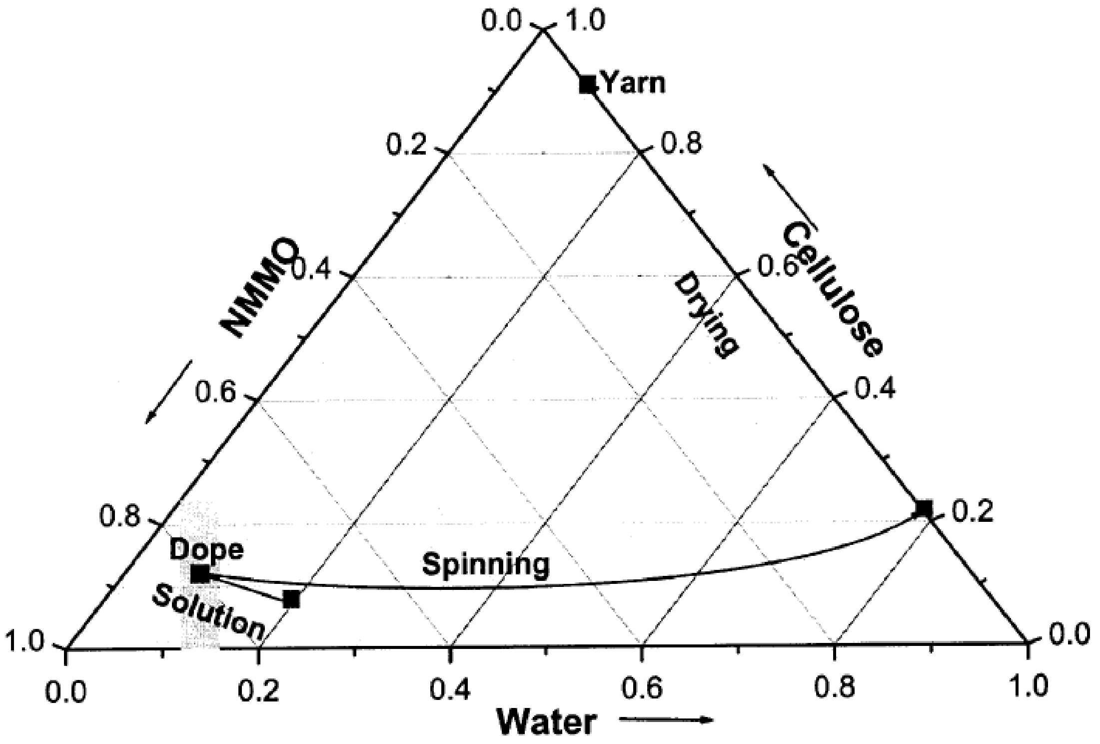
Cellulose dissolution



- N-O bond forms strong hydrogen bonds with cellulose, capable of breaking its hydrogen bonding network
- Produces isotropic solutions of cellulose up to ~21% concentration in the temperature interval 72-120°C

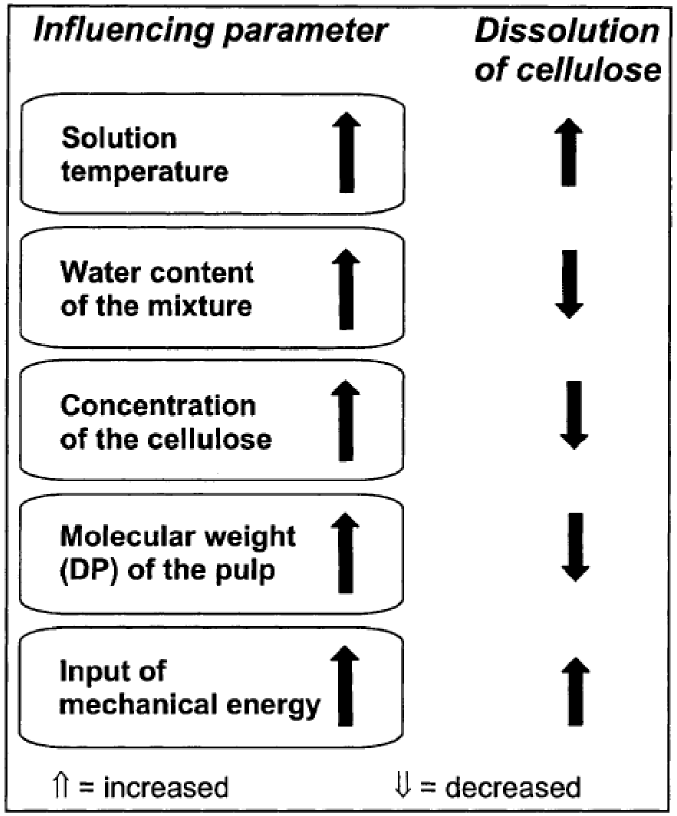
NMMO

Phase diagram of NMMO/water/cellulose



Rosenau et al. *Prog. Polym. Sci.* **2001**, *26*, 1763.

NMMO



Influencing parameter		Dissolution of cellulose
Solution temperature	↑	↑
Water content of the mixture	↑	↓
Concentration of the cellulose	↑	↓
Molecular weight (DP) of the pulp	↑	↓
Input of mechanical energy	↑	↑

⇑ = increased ⇓ = decreased

Qualitative factors influencing cellulose dissolution in NMMO

Rosenau et al. *Prog. Polym. Sci.* **2001**, *26*, 1763.

Presemo

Take out your smartphones or laptops and type:

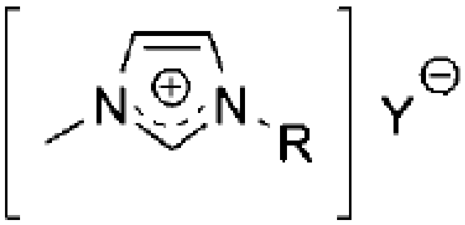
http://presemo.aalto.fi/e2140dissol

Ionic liquids

- Ionic liquid is a salt that melts below 100°C
- Very low vapour pressure
- High thermal stability
- High solvation ability
- Can be easily modified by changing the structure of the cations or anions

Ionic liquids

Structures for ionic liquids with 1-alkyl-3-methylimidazolium cation, typical cellulose solvents



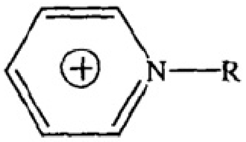
$R=CH_3$: $[C_1mim]$; $R=CH_3CH_2$: $[C_2mim]^+$
$R=CH_3CH_2CH_2$: $[C_3mim]^+$
$R=(CH_3)\,_2CH_2$: $[C_3mim]^+$
$R=CH_3CH_2CH_2CH_2$: $[C_4mim]^+$
$R= CH_3CH_2CH_2CH_2CH_2CH_2$: $[C_6mim]^+$
$R= CH_3CH_2CH_2CH_2\ CH_2CH_2CH_2CH_2$: $[C_8mim]^+$
$R= CH_2{=}CHCH_2$: $[Amim]^+$

- The charges are distant from each other because of the bulky ”shell” around the cations formed by neutral atoms
- The shell reduces the energy of electrostatic interactions between the ions
- The electrostatic energy becomes less than the energy of thermal motion of the ions at low temperatures

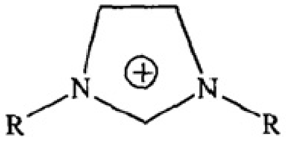
→ Crystallization is prevented and the substance is fluid

Ionic liquids

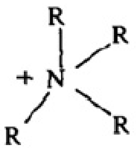
Examples of diverse ionic liquid structures



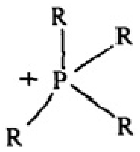
N-alkyl pyridine cation



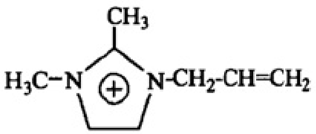
N, N-2-alkyl imidazole cation



alkyl quaternary ammonium cation



alkyl quaternary phosphonium cation



$[Admin]^+$

[HEmin]

PF_6^-: hexafluorophosphate BF_4^-: tetrafluomborate

C1$^-$, I^-: halides CF_3COO^-: trifluoroacetate(TA.)

Ionic liquids

Dissolution of cellulose by ionic liquids

- Ability to dissolve cellulose (with 1-butyl-3-methyl imidiazole) first reported in 2002 (Swatloski et al. *J. Am. Chem. Soc.* **2002**, *124*, 4974)
- Nowadays an extremely viable research area

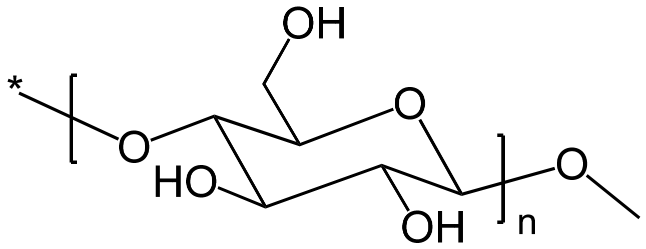
Used for:

  - Chemical modification of cellulose
  - Degradation of cellulose
  - Preparing various regenerated grades

Note: No industrial applications as of yet.

Ionic liquids

Mechanism of cellulose dissolution



- The anions interact directly with cellulose hydroxyl groups (simple anions: acetate, formiate, Cl^- etc.)
- The anions must be good hydrogen bond acceptors
- Excess of anions is required: 1.5-2.5 anions / hydroxyl group for dissolution
- There is no evidence of the interactions between cations (in ionics liquids) and cellulose

Wang et al. *Chem. Soc. Rev.* **2012**, *41*, 1519.

Ionic liquids

Parameters for cellulose dissolution

Anions

- Cellulose **cannot** be dissolved in ionic liquids with non-coordinating anions (e.g., BF_4^- or PF_6^-)
- The higher the hydrogen bond basicity and dipolarity, the greater the ability of salts of that anion to dissolve cellulose
- For example, a larger amount of cellulose can be dissolved in 1-allyl-3-methylimidazolium formate than the corresponding chloride (hydrogen bonding basicity of formate is 1.2 fold higher than that of chloride)

Solubility increases with increasing hydrogen bond accepting ability:
$OAc^- > HSCH_2COO^- > HCOO^- > (C_6H_5)COO^- > HOCH_2COO^- > CH_3CHOHCOO^-$

Wang et al. *Chem. Soc. Rev.* **2012**, *41*, 1519.

Ionic liquids

Parameters for cellulose dissolution

Cations

- Although cations are probably not *directly* involved in the interactions with cellulose, they play a major role in the dissolution
- When the alkyl chain length in the cation is increased, the solvent power of ionic liquids is generally decreased (speculatively attributed to reduced effective chloride concentration)
- However, cellulose is more soluble in 1-alkyl-3-imidazolium-based ionic liquids with even-numbered alkyl chains compared with odd-numbered ones (below six carbon units)

NOTE: The role of cations is controversial in the light of current research.

Wang et al. *Chem. Soc. Rev.* **2012**, *41*, 1519.

Ionic liquids

Influence of cellulose source on dissolution

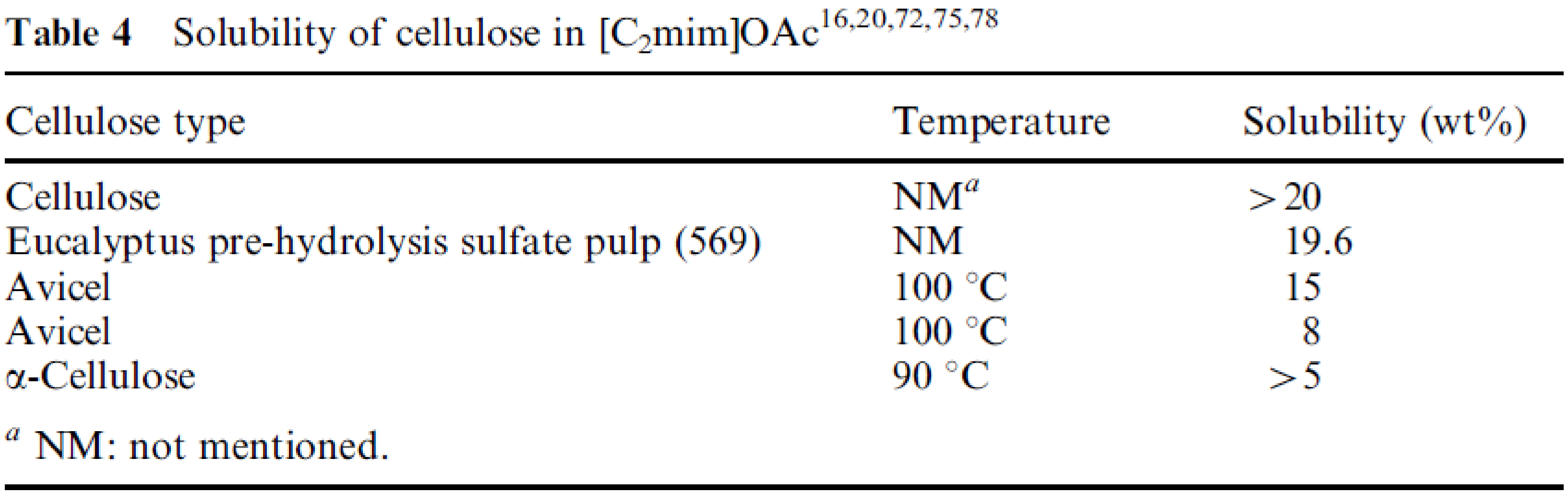


Table 4 Solubility of cellulose in $[C_2mim]OAc$[16,20,72,75,78]

Cellulose type	Temperature	Solubility (wt%)
Cellulose	NM[a]	> 20
Eucalyptus pre-hydrolysis sulfate pulp (569)	NM	19.6
Avicel	100 °C	15
Avicel	100 °C	8
α-Cellulose	90 °C	> 5

[a] NM: not mentioned.

- Source affects the solubility but no clear explanation can be provided

Wang et al. *Chem. Soc. Rev.* **2012**, *41*, 1519.

Ionic liquids

NOTE: Dissolution of cellulose in ionic liquids, its modification therein, and the regeneration thereof is one of the most active research areas with renewable materials at present.

Many fundamental details on cellulose dissolution in ionic liquids remain elusive.

Some literature reviews:
Li et al. *Chem. Sci.* **2018**, *9*, 4027.
Yoo et al. *Curr. Opin. Green Sustainable Chem.* **2017**, *5*, 5.
Wang et al. *Chem. Soc. Rev.* **2012**, *41*, 1519.
Pinkert et al. *Chem. Rev.* **2009**, *119*, 6712.
Feng and Chen *J. Mol. Liq*. **2008**, *142*, 1.

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Summary: general considerations

On solvent

- No general theory exists on why a certain compound is a cellulose solvent

On the cellulose substrate

- At present, the consensus is that neither molecular weight nor the crystallinity of cellulose determines fully the solubility of cellulose in its solvents

- Some reports discuss the hierarchical fibre morphology as a possible determining factor for solubility (long-range interactions, see, e.g., Le Moigne and Navard *Cellulose* **2010**, *17*, 31.)