

Theory and Practice of Wet Spinning of Cellulose Solutions

Doctoral Course, **Part 4**



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School of Chemical
Engineering

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March 10 – 11, 2022

Outline

1. Introduction, history
2. Pulps as raw materials
3. Cellulose solvents
- 4. Aspects of cellulose dissolution**
- 5. Rheology of cellulose solutions**
- 6. Coagulation and regeneration of cellulose**
- 7. Filament breaches during spinning**
- 8. Types of MMCFs**
- 9. Properties of MMCFs**

Schedule

L1	Introduction, Raw material	March 10	9:00 – 9:45
L2	Raw materials. Cellulose solvent	March 10	10:00-10:45
L3	Cellulose solvents	March 10	11:00-11:45
L4	Cellulose solvents	March 10	12:00-12:45
	Break		
L5	Cellulose dissolution	March 10	14:00-14:45
L6	Rheology	March 10	15:00-15:45
L7	Cellulose dissolution/ Coagulation and Regeneration	March 10	16:00-16:45
L8	Coagulation and Regeneration	March 11	9:00 – 9:45
L9	Coagulation and Regeneration	March 11	10:00-10:45
L10	Filament breaches	March 11	11:00-11:45
L11	Types and properties of MMCFs	March 11	12:00-12:45
L12	Q&A	March 11	13:00 -

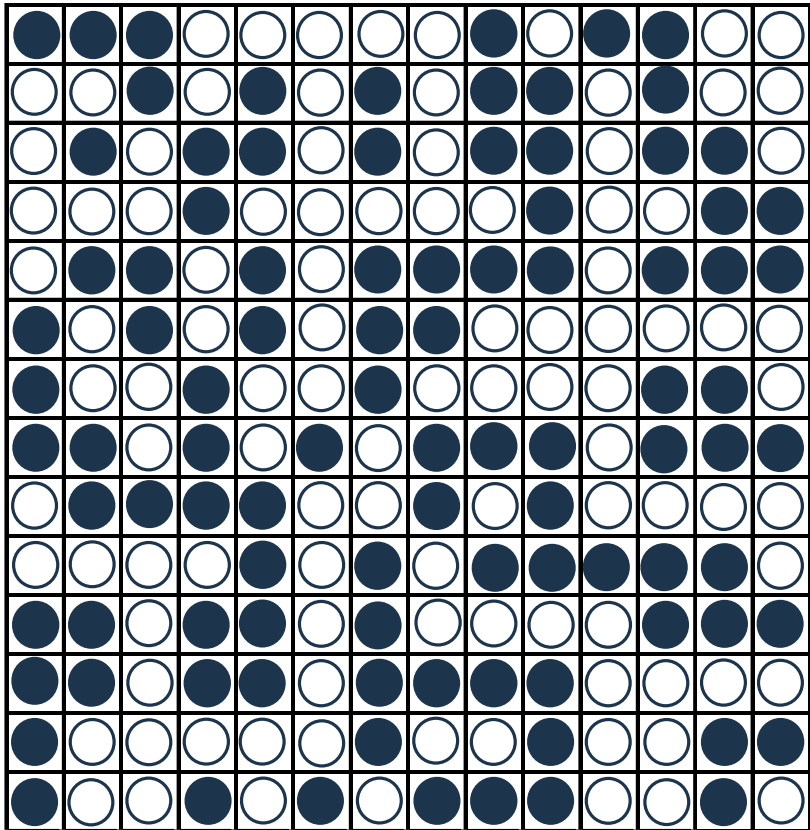
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Aspects of cellulose dissolution

- **Thermodynamics of polymer solutions**
- **Solubility parameters**
- **Solution structure**
- **MD of NMMO/water/cellulose system**

Regular Solution Theory

2-D Square Lattice with each site occupied by either of two species



Mixing a solute and solvent with equal size and intermolecular interactions: Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S$$

No change in enthalpy: $\Delta H_m = 0$;

Increase in disorder: $\Delta S_m > 0$; therefore

$\Delta G_m < 0$ to achieve spontaneous mixing.

Entropy of Mixing

$$S = k \ln \Omega \text{ (Boltzmann)}$$

Configurational entropy for each pure component is zero: $S_1 = k \ln \Omega_1 = S_2 = k \ln \Omega_2 = 0$

Ω total number of possible configurations that the system can adopt \Rightarrow thermodynamic probability

N_1, N_2 number of solvent and solute molecules

N sites of total number of configurations and thus

$$\Omega = N! / (N_1! N_2!)$$

$S_m = k \{ \ln N! - \ln N_1! - \ln N_2! \}$ With Stirling, $\ln N! \approx N \ln N - N$:

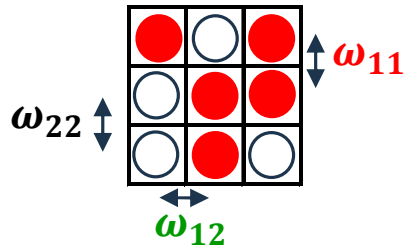
$S_m = -k \{ N_1 \ln(N_1/N) + N_2 \ln(N_2/N) \} \Rightarrow$ multiply by N_A results in: $S_m = -R(x_1 \ln x_1 + x_2 \ln x_2)$

$$\Delta S_m = S_m - S_1 - S_2 = -R (x_1 \ln x_1 + x_2 \ln x_2)$$

ΔS_m is the **configurational entropy, entropy of mixing**

Enthalpy of Mixing a Regular Solution

**Neighbor interactions, ω_{ij} ,
energies of a mixture**



$$\Delta H_m = \Delta U_m \text{ (if } V, P \text{ are constant)}$$

Interaction of molecules via dispersion forces.

Thus, ω_{11}, ω_{22} are negative

(ΔH_m proportional to energy difference through polymer-polymer, solvent-polymer, solvent-solvent contacts x the number of contacts):

$$H_1 = \frac{1}{2} n_1 z \omega_{11}$$

$$H_2 = \frac{1}{2} n_2 z \omega_{22}$$

z neighbors, z interactions;

Only one ω_{11} interaction energy per *pair* of molecules (divide by 2)

Molecules interact only with the nearest neighbors

Enthalpy of Mixing of a Regular Solution

Probability that a neighboring site is occupied by a molecule of type 1 or 2 is x_1, x_2

$$H_m = \frac{1}{2} n_1 (z x_1 \omega_{11} + z x_2 \omega_{12}) + \frac{1}{2} n_2 (z x_1 \omega_{12} + z x_2 \omega_{22})$$

$$\Delta H_m = H_m - H_1 - H_2 \Rightarrow \Delta H_m = \frac{n_1 n_2}{n} z \Delta \omega$$

$$\Delta \omega = \left(\omega_{12} - \frac{\omega_{11}}{2} - \frac{\omega_{22}}{2} \right) = \text{Exchange Energy}^*$$

$\Delta \omega \geq 0$ for dispersion forces and for the regular solution theory

$$\chi \equiv \frac{z \Delta \omega}{kT} \quad \chi = \text{Interaction parameter: exchange energy per molecule}$$

$$\Delta H_m = x_1 x_2 \chi RT \quad \dots \text{ per mole} \quad \text{with } \Delta G_m = \Delta H_m - T \Delta S_m$$

$$\frac{\Delta G_m}{RT} = (x_1 \ln x_1 + x_2 \ln x_2 + x_1 x_2 \chi) \quad \dots \text{ per mole}$$

*(Cross-interactions – self interactions)

Free Energy of Mixing - Example

Mixing 1 mol of toluene with 1 mole of cyclohexane at room temperature:

$$\omega_{11} = -1.17 \times 10^{-20}; \omega_{12} = -1.08 \times 10^{-20}; \omega_{22} = -1.01 \times 10^{-20} J$$

$z = 10$ (coordination number = nearest neighbors)

$$\chi = \frac{z\Delta w}{kT} \approx \frac{10}{1.38 \cdot 10^{-23} \cdot 298} \left\{ -1.08 + \frac{1.17 + 1.01}{2} \right\} \cdot 10^{-2} = \mathbf{0.24}$$

$$\frac{\Delta G_m}{RT} = (n_1 \ln x_1 + n_2 \ln x_2 + n_1 x_2 \chi)$$

$$n_1 = n_2 = 1, x_1 = x_2 = 0.5$$

$$\Delta G = [\ln(0.5) + \ln(0.5) + (0.5 * 0.24)] \cdot 298 \cdot 8.3145 \cdot 2 = \mathbf{-6.28 kJ}$$

Spontaneous mixing of toluene with cyclohexane even though χ is positive.

Flory-Huggins Theory

Attempts to describe the thermodynamics of polymer solutions, to account for intermolecular interactions

Assumptions:

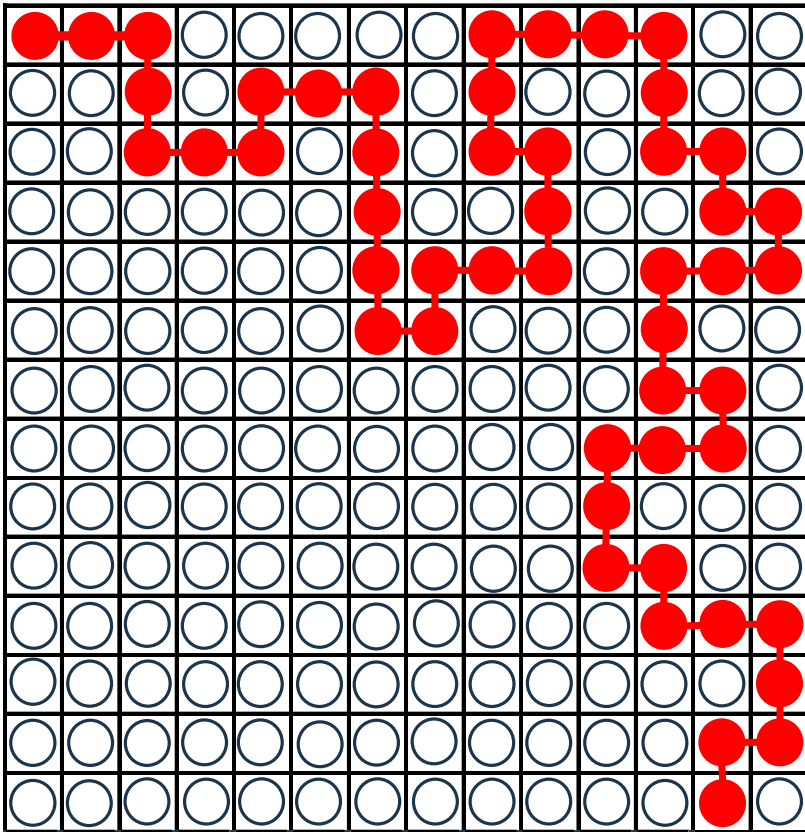
- No volume change on mixing, independent on concentration, random mixing
- Local concentration given by bulk average composition (= mean-field assumption)
- ΔS_m is the ideal combinatorial entropy of mixing, ΔH_m is the internal energy of mixing
- Interactions are short-ranged and pairwise additive.
- A polymer has a bunch of segments, where each segment is the size of the solute.

Flory's combinatorial entropy of mixing:

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

where ϕ_1 (solvent) and ϕ_2 (polymer) are the **volume fractions**

Flory-Huggins – Entropy of Mixing



Volume of one solvent molecule occupies one lattice site (1), each polymer (2) N lattice sites ($N \propto DP$) $\Rightarrow V_{Solvent} \approx V_{Monomer}$

$$\phi_1 = \frac{n_1}{n_1 + Nn_2} \quad \phi_2 = \frac{Nn_2}{n_1 + Nn_2}$$

$\phi_{1/2}$...volume fractions of solvent & polymer

$$\phi_1 = \frac{146}{146+50 \cdot 1} = 0.74 \quad \phi_2 = \frac{50 \cdot 1}{146+50 \cdot 1} = 0.26$$

$$\Delta S_m = -R[n_1 \ln \phi_1 + n_2 \ln \phi_2] = -8.314 \cdot [146 \cdot \ln 0.74 + 1 \cdot \ln(0.26)] = 369 J$$

[Example: 10 g toluene with 92 g/mol MM mixing with 10 g PS (0.109 mol) with 10^5 g/mol MM (0.0001 mol) and 104 g/mole of PS monomer \Rightarrow volume fraction = $10^5/104 = 962$:

$$\phi_{1(solvent)} = \frac{0.109 \text{ mol}}{0.0001 \text{ mol} \cdot 962 + 0.109 \text{ mol}} = 0.531$$

$$\phi_{2(polymer)} = \frac{(0.0001 \text{ mol}) \cdot 962}{0.0001 \text{ mol} \cdot 962 + 0.109 \text{ mol}} = 0.469$$

$$\Delta S_m = -8.314[0.109 \ln(0.531) + 0.0001 \ln(0.469)] = 0.574 J$$

Flory, P.J., *J.Chem.Phys.* (1942), 10, 51.

Huggins, M.L., *J.Am.Chem.Soc.* (1942), 64, 1712.

Flory-Huggins: Enthalpy of Mixing

Enthalpy of mixing in Flory-Huggins theory: substitutions of ϕ_1 and ϕ_2 for x_1 and x_2

$$\Delta H_m = n_1 \phi_2 \chi RT \quad \text{for the system}$$

$$\Delta H_m = \phi_1 \phi_2 \chi kT \quad \text{per site}$$

Combining the expressions for ΔS_m and ΔH_m for the system:

$$\frac{\Delta G_m}{RT} = (n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi) \left[\frac{\Delta G_m}{RT} = \left(\phi_1 \ln \phi_1 + \frac{\phi_2}{N} \ln \phi_2 + \phi_1 \phi_2 \chi \right) \right] \text{ per site}$$

Entropy terms always favor mixing, the enthalpy opposes mixing when $\chi > 0$.

Limitation: model assumes that local concentration is uniformly throughout the sample (*mean-field assumption*). However, model gets progressively better when concentration is increased and coils start to interpenetrate.

Osmotic Pressure: Flory-Huggins

$$\text{Chemical potential: } \mu_i = \left(\frac{\delta G}{\delta n_i} \right)_{p,T,n_{i \neq j}} \Rightarrow -\Pi \bar{V}_1 = \mu_1^0 - \mu_1 = \left(\frac{\delta}{\delta n_1} \Delta G_m \right)_{p,T,n_2} = \frac{\delta}{\delta n_1} \{RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi)\}$$

$$\Rightarrow \Rightarrow \frac{\Pi \bar{V}_1}{RT} = - \left\{ \ln(1 - \phi_2) + \phi_2 \left(1 - \frac{1}{N} \right) + \chi \phi_2^2 \right\} \quad \text{with} \quad \ln(1 - \phi_2) = -\phi_2 - \phi_2^2/2 \Rightarrow \Rightarrow \Rightarrow$$

$$\frac{\Pi}{RT} = \frac{c}{M} + \left(\frac{1}{2} - \chi \right) \frac{\bar{V}_2^2}{\bar{V}_1} \frac{1}{M^2} c^2 + B_3 c^3 + \dots$$

$$\left(\frac{1}{2} - \chi \right) \frac{\bar{V}_2^2}{\bar{V}_1} \frac{1}{M^2} = B$$

$\bar{V}_1, \bar{V}_2 \dots$ partial molar volume. **B** second virial coefficient

Osmotic pressure measurements on dilute solutions allows M_n and **B measurements**

$\chi = 0.5 \Rightarrow B = 0$ **Theta solvent** where polymer-solvent interactions rather poor; no swelling; random walk

$\chi < 0.5 \Rightarrow B > 0$ Good solvent, chain swells, $R_g \sim M^{3/5}$

Semiempirical solubility parameter from χ

$$\chi = \frac{z\Delta w}{kT} \quad (1)$$

For London dispersion interactions, the interaction energy is

$$w_{ij} \sim -\frac{\alpha_i \alpha_j}{r_{ij}^6}; \quad \alpha_i \dots \text{polarizability of molecule } i. \quad (2)$$

If we have a lattice where, $r_{ii} = r_{jj} = r_{ij}$, then: (3)

$$w_{12} = -\frac{\alpha_1 \alpha_2}{r_{12}^6} = -\frac{\alpha_1}{r_{11}^6} \frac{\alpha_2}{r_{22}^3} = -\sqrt{w_{11} w_{22}} \quad (4)$$

$$z\Delta w = z \left(\omega_{12} - \frac{\omega_{11}}{2} - \frac{\omega_{22}}{2} \right); \text{ with (4)}$$

$$z\Delta w = \frac{z}{2} \left[\sqrt{w_{11}} - \sqrt{w_{22}} \right]^2 \quad (5)$$

Molar heat of vaporization for pure substance,

$$\hat{U}_{vap} = -N_A \frac{zw_{11}}{2} \quad (6)$$

interaction energy lost by removing one i molecule from the substance

$$\text{Cohesive energy density: } \delta_i^2 = \frac{\hat{U}_{vap}}{\hat{V}_i} = \frac{\Delta H_v - R}{\hat{V}_i} - N_A \frac{zw_{11}}{2\hat{V}_i} \quad (7)$$

From (1), (5) and (7)

$$\chi = \frac{\hat{V}_1}{RT} (\delta_1 - \delta_2)^2 \quad (8)$$

Hildebrand solubility parameter

$$\delta = \sqrt{\frac{\Delta H_v - RT}{\hat{V}_i}}$$

\hat{V}_1 actual volume of a polymer segment
= solvent size

δ_1 solubility parameter of the solute

δ_2 solubility parameter of the solvent

δ in $(MPa)^{0.5}$ or $cal^{0.5} cm^{-1.5}$

with $1 (MPa)^{0.5} \equiv 2.0455 (cal^{0.5} cm^{-1.5})$

χ Example

Polystyrene ($\delta = 9.1 \text{ cal}^{0.5} \text{ cm}^{-1.5}$) in Cyclohexane ($\delta = 8.2 \text{ cal}^{0.5} \text{ cm}^{-1.5}$) at 34.5°C where Cyclohexane is a theta solvent, where $\chi = 0.5$ [$\hat{V}_1 \approx M/\rho$; $R = 1.987 \text{ cal/K}$]

$$\chi = \frac{84/0.78}{1.987 \cdot 307.6} (9.1 - 8.2)^2 \approx 0.14 \quad \hat{V}_1 = M/\rho$$

$\chi = 0.5 \neq 0.14$ \Rightarrow the possibility of H-bonding invalidates basic assumptions

Empirical equation for χ in case predicted value of $\chi < 0.3$

$$\chi = 0.34 + \frac{\hat{V}_1}{RT} (\delta_1 - \delta_2)^2$$

The 0.34 term shows no T-dependence, thus it is an additional entropy of mixing contribution

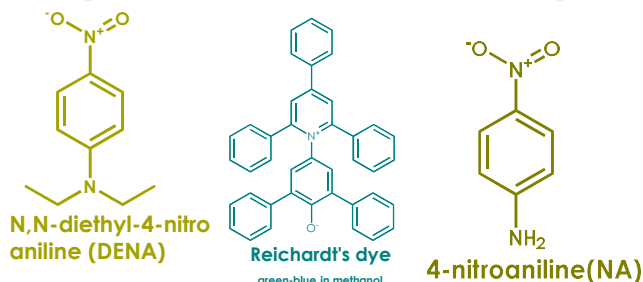
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Aspects of cellulose dissolution

- Thermodynamics of polymer solutions
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Kamlet Taft Parameters

Empirical Solvent descriptor



π^* ...Dipolarity / polarizability

$$\pi^* = 0.314 (27.52 - \nu_{DENA})$$

Measures the ability of a solvent to stabilize a charge or a dipole through its dielectric effect

$E_T(30)$...Solvent polarity

$$E_T(30) = \frac{28591}{\lambda_{max}} (nm), kcal \cdot mol^{-1}$$

Charge-transfer absorption band of Reichard's dye indicating overall interactions between solvent and the dye

α ...H-bond acidity (donor)

$$\alpha = 0.0649 \cdot E_T(30) - 2.03 - 0.72\pi^*$$

Ability to donate a proton in a solvent to solute H-Bond: Availability of H-donor sites on the cation

β ...H-bond basicity (acceptor)

$$\beta = \frac{(1.035 \nu_{DENA} + 2.64 - \nu_{NA})}{2.80}$$

Measure of the solvent's ability to accept a proton in a solute-to-solvent H-bond

Y.Fukuya, A.Sugimoto, H. Ohno. Biomacromolecules, 7, 12 (2006)

M.J. Kamlet, J-L.M. Abboud, MH: Abraham, R.W.Taft, JOGS, 48, 2877-2887 (1983)

Example: KT of [emim]OAc at 20°C

Dyes	C, mg/mL	Spectral maxima, nm
RD	0.624	570.25
DENA	0.038	404.35
NA	0.047	411.53

$$E_T(30) = \frac{28592}{570.2} = 50.1$$

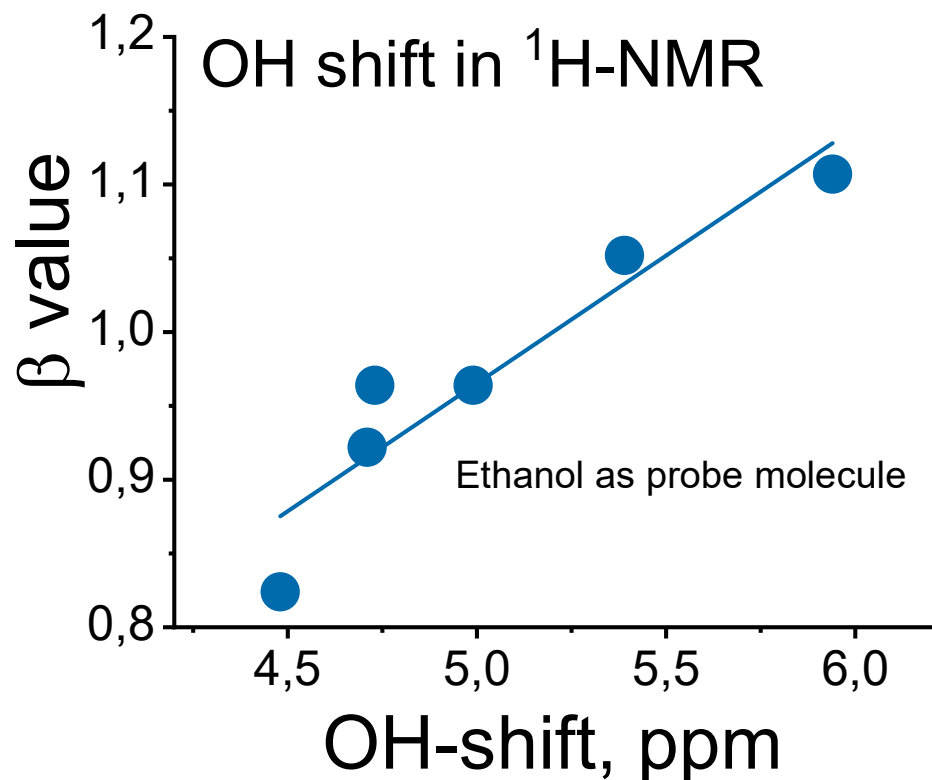
$$\pi^* = 0.314 \left(27.52 - \frac{10^4}{411.5} \right) = 1.011$$

$$\alpha = 0.0649 \cdot 50.1 - 2.03 - (0.72 \cdot 1.011) = 0.494$$

$$\beta = \frac{\left(1.035 \cdot \frac{10^4}{411.5} + 2.64 - \frac{10^4}{404.4} \right)}{2.8} = 1.094$$

β -scale

Anions' interactions with the OH groups of the AHG unit as the main driving force for cellulose dissolution.



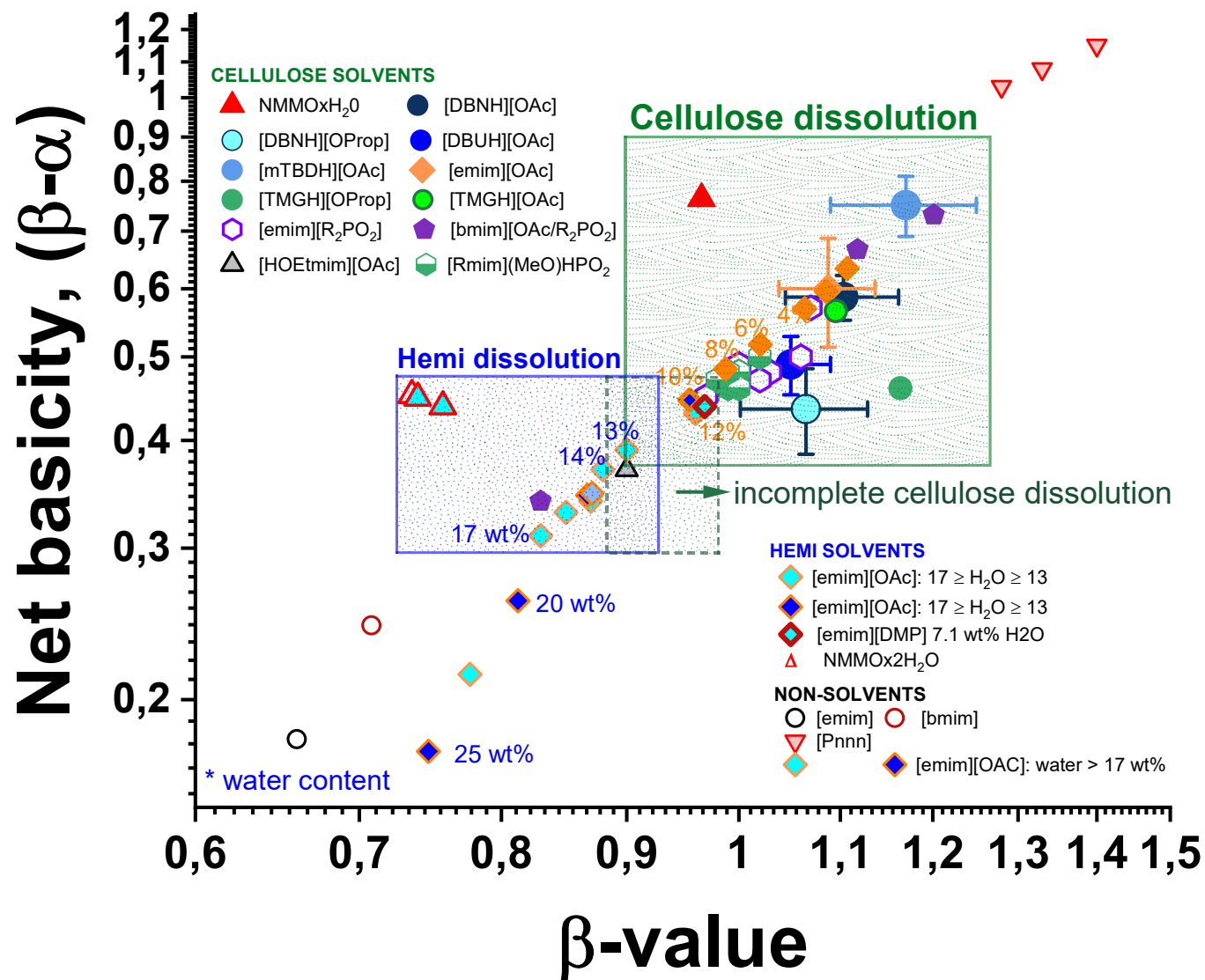
Difference between the chemical shifts of the ethanol- CH_3 and the ethanol-OH resonances in different neat ILs:

[emim][OAc], [BMIM][dmp], [BMIM][dmpt] (2X), [AMIM][dmp], [BMIM][dmpSe]

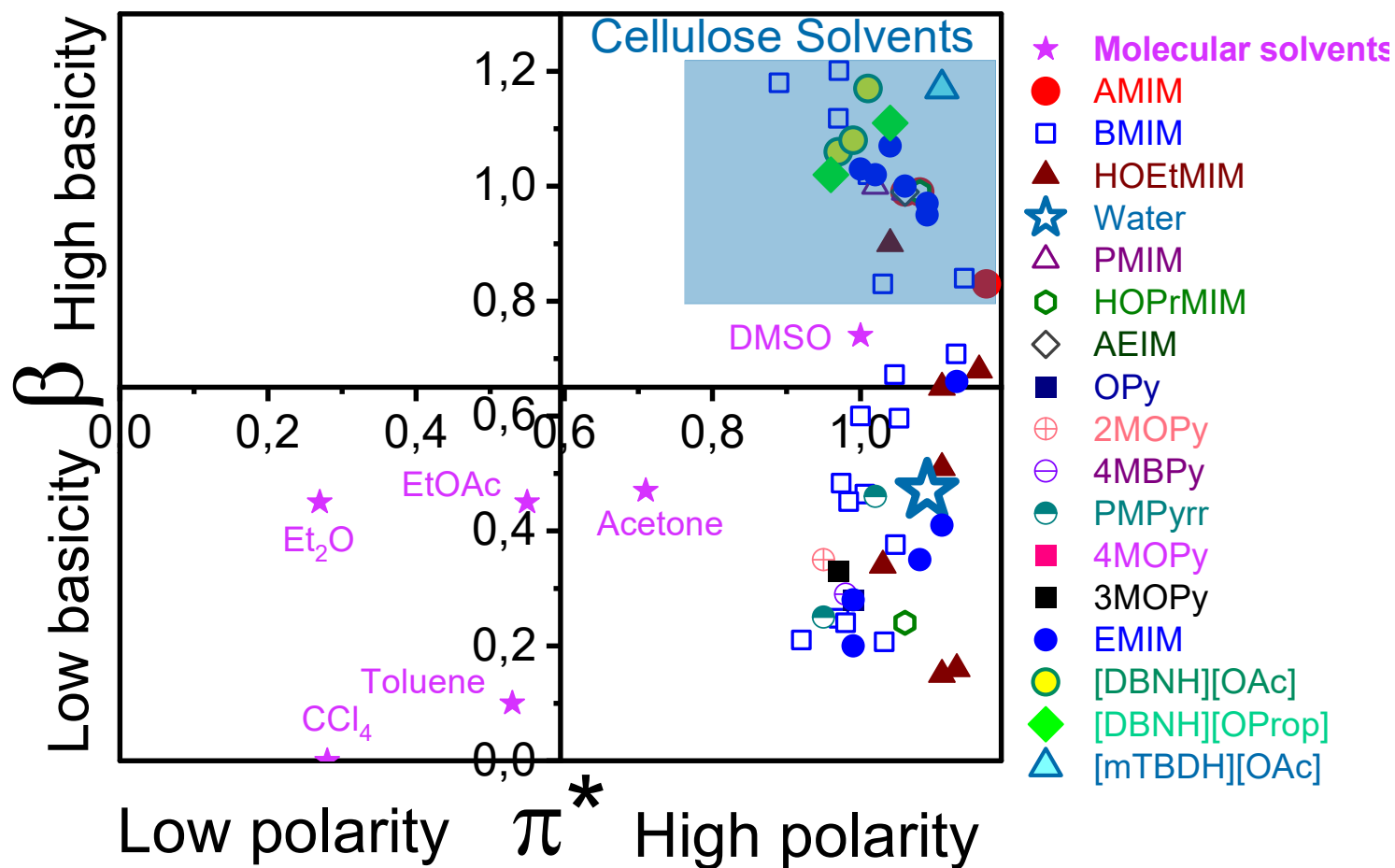
Kamlet-Taft

Empirical solubility parameters to identify solvents for the dissolution of **Cellulose** and **Hemicellulose**

M.J. Kamlet and R.W. Taft: JACS, 98:2, 377-383 (1976)
 R.W. Taft and M.J. Kamlet: JACS, 98:10, 2886-2894 (1976)



Polarity-Basicity (β) Plots



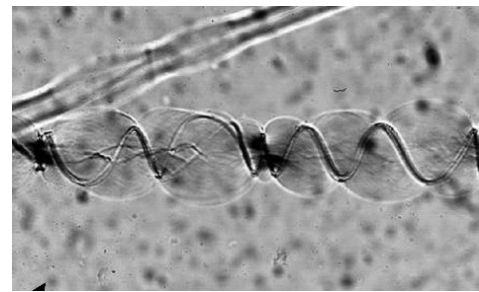
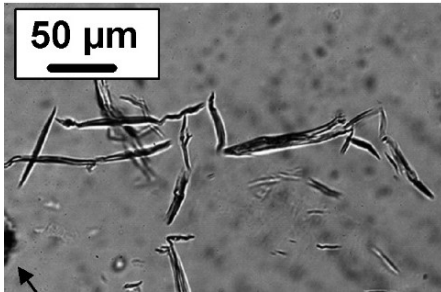
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Aspects of cellulose dissolution

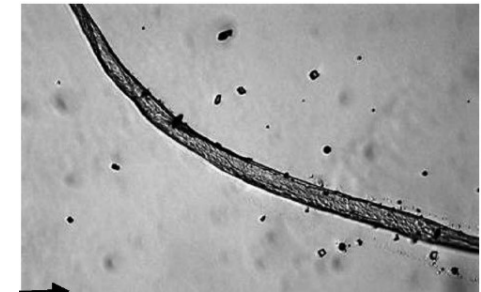
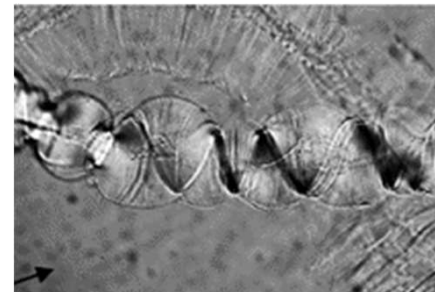
- Thermodynamics of polymer solutions
- Solubility parameters
- **Solution structure**
- **MD of NMMO/water/cellulose system**

Modes of Solvent Cellulose Interaction

Dissolution



Partial-, Non-Solvent



Fragmentation

Ballooning

Ballooning

Homogeneous swelling

Good quality
H₂O < 17 wt% in
NMMO

Moderate quality
H₂O 18-24 wt% in
NMMO

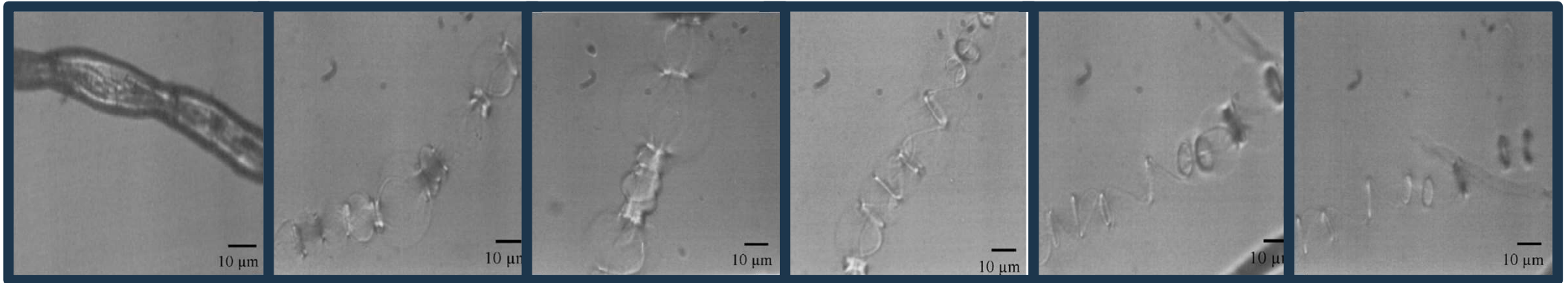
Bad quality
H₂O 25-35 wt% in
NMMO

Non-Solvent

No complete
dissolution

No dissolution

Sulfite pulp in NMMO with 19 wt% water



Fibre begins
To swell

First balloons
appear

Balloons
grow

Maximum
diameter
reached

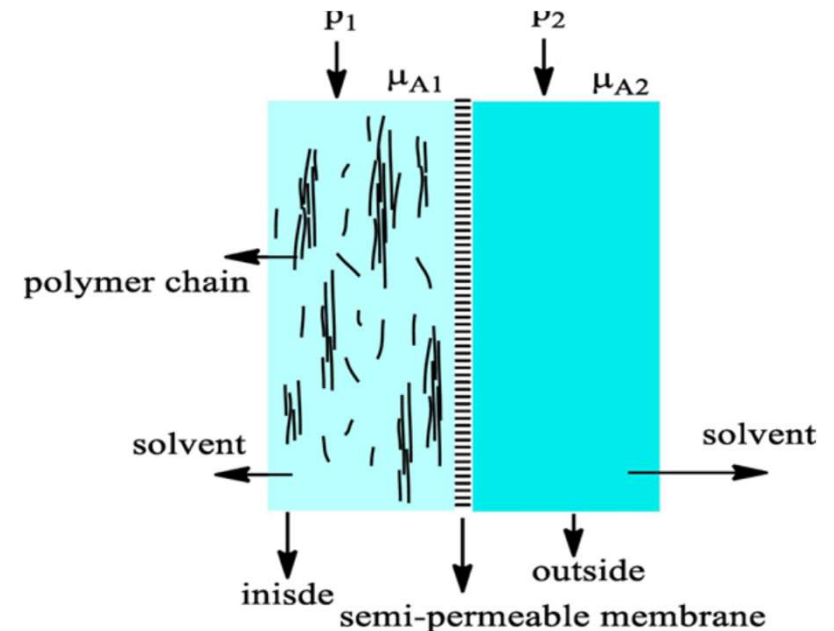
First balloons
burst

All balloons
have burst

PW not easy to be dissolved compared to **S2** wall in the NMMO / water system

S2 wall contains hydrophilic OH \rightarrow
H₂O can penetrate into **S2** layer \rightarrow
Solvent molecules penetrate into cellulose **under increasing osmotic pressure**

The solvent concentration in the first outer layer gradually increases \rightarrow
At a certain solvent concentration fiber interior starts to dissolve

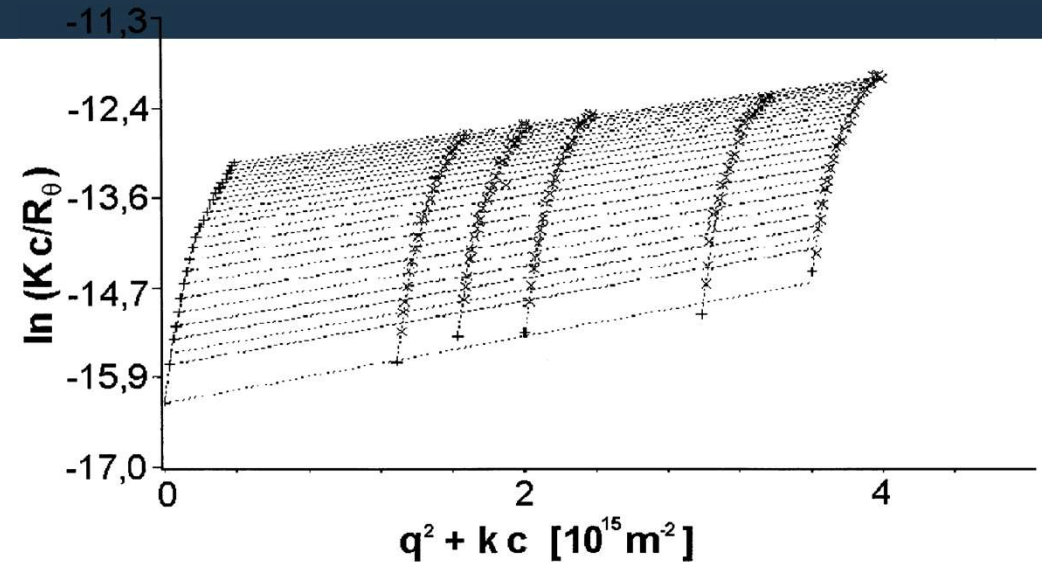


If the osmotic pressure is greater than the resistance of the **PW** at a certain point in time, the **membrane bursts**, otherwise swelling stops.

Cellulose solution structure in NMMO



- Fringed micelle
- Interpenetrated network solution
- $R_g \sim 100 - 200 \text{ nm}$
- **NMMO*H₂O: $R_g = 188 \text{ nm}$**



$$\frac{K_c}{R_\theta} = \frac{1}{M_w P_q} + 2A_c \cdot c + \dots$$

$$P_q^{-1} = \exp\left(\frac{1}{3} q^2 R_g^2\right)$$

For globular structures

Guinier-Zimm plot:

$\ln(K_c/R_\theta)$ is plotted against $(q^2 + kc)$
($c \rightarrow 0$) and ($q \rightarrow 0$)

Effect of water in IL on solution structure

Water-free

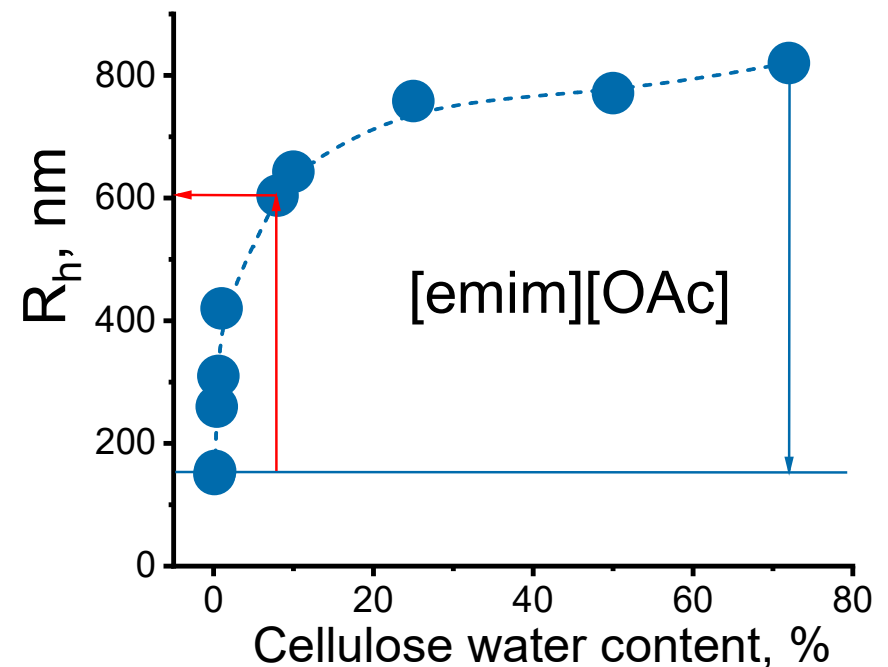
R_g , radius of gyration = 101 nm \rightarrow \sim 4 times the size of a fully solvated molecule \rightarrow aggregate solution; $n_{\text{aggregate}} \sim 21$. Still, much lower than in the case of NMMO.

R_h , hydrodynamic radius accessible from DLS, Stokes radius: $R_h = \frac{k_B T}{6\pi\eta D}$

In presence of water

Size of cellulose aggregates grows with an increase in water content.

Limit for [emim][OAc] about 8% water as for a cellulose solvent.



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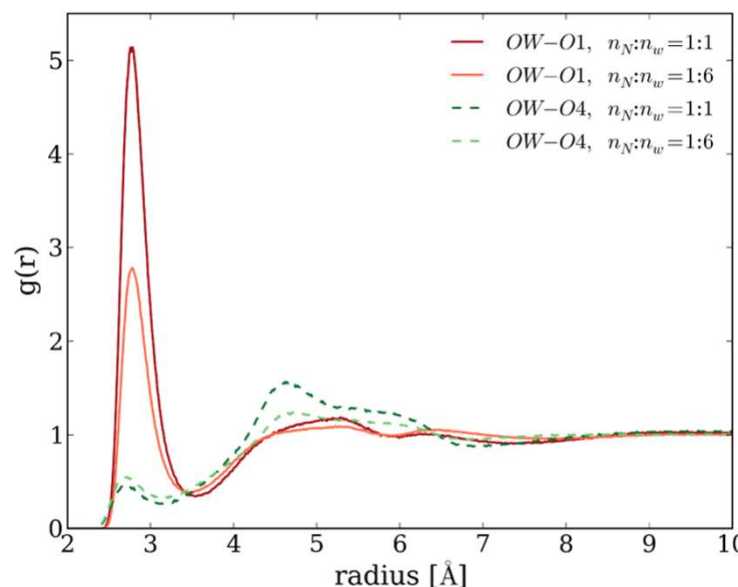
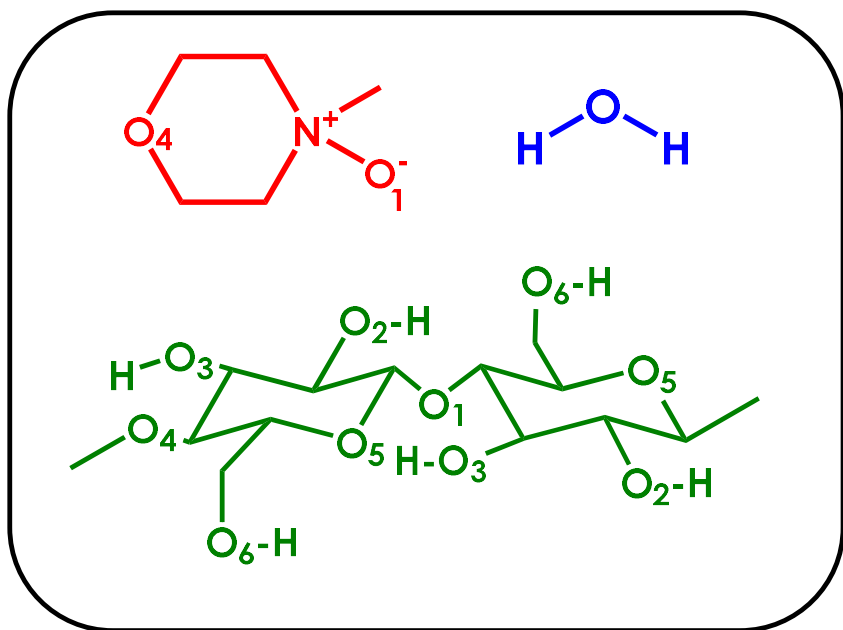
Aspects of cellulose dissolution

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Dissolution of Cellulose in NMMO: Effect of water content

All-atom MD with algorithms for short-range molecular dynamics to study ternary systems of cellulose (DP 12), NMMO and water.

Radial distribution functions (RDF) between water-O (OW) and O atoms (O1, O4) of NMMO

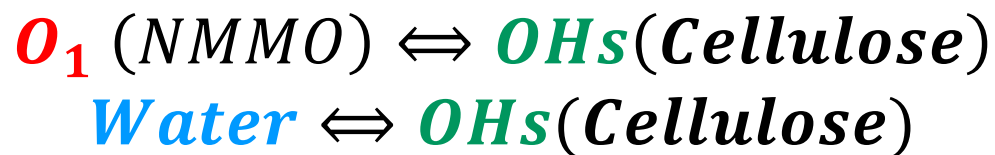


Strong association of water with the O1 of NMMO at 2.8 Å;

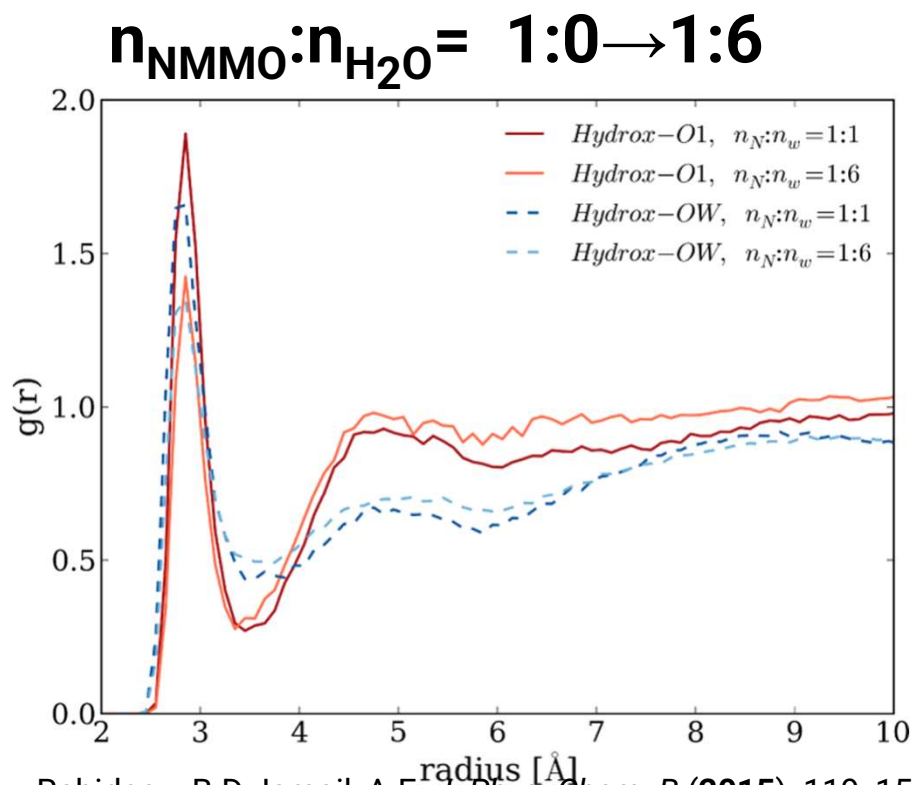
weaker association with O4

O1 good H-bond acceptor, Water a good H-bond donor

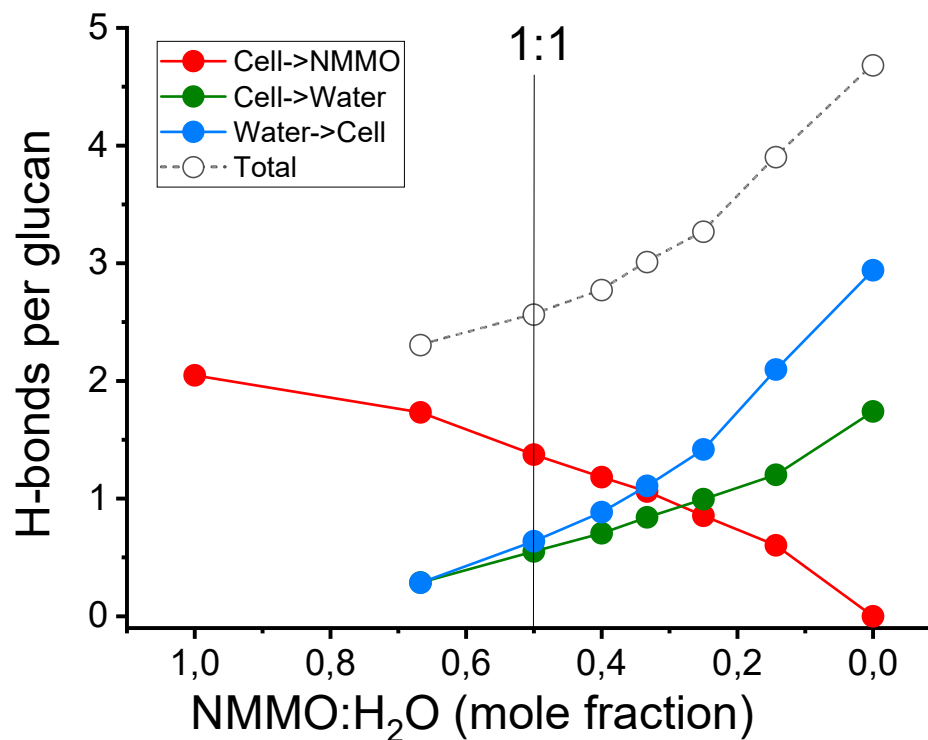
RDFs between Cellulose, NMMO and Water



OH groups of cellulose are strongly attracted to both water oxygens and the O1 (NMMO)

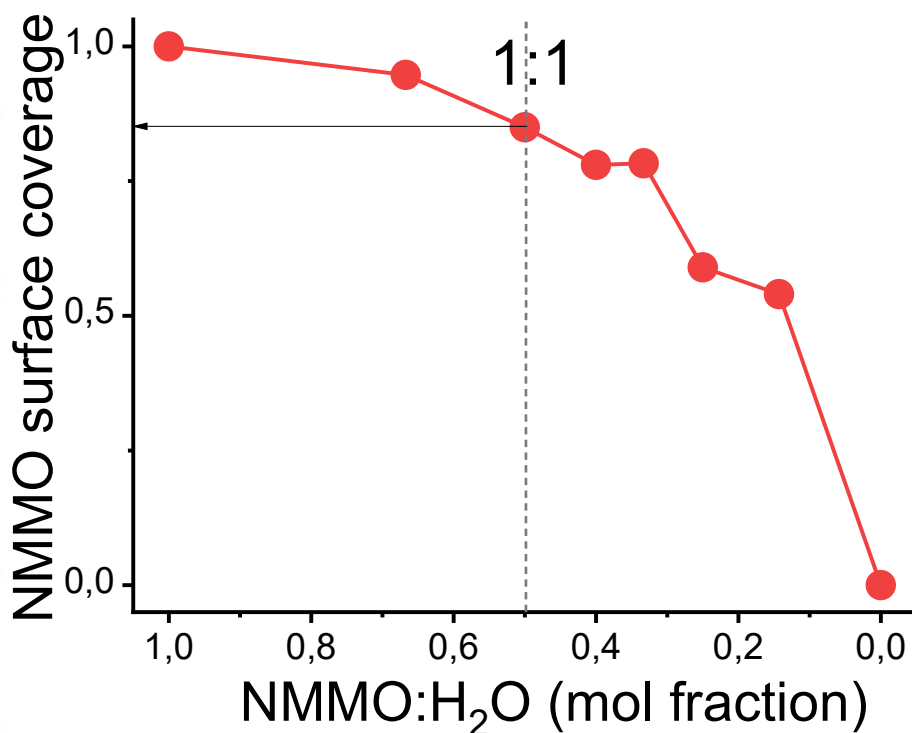
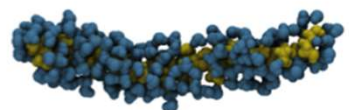
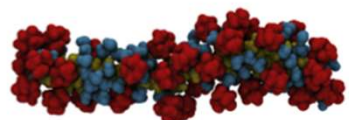
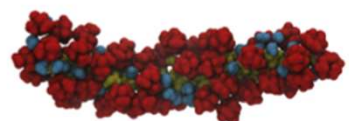
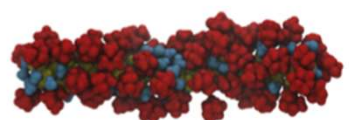
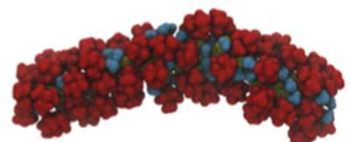
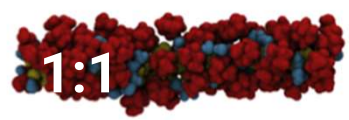
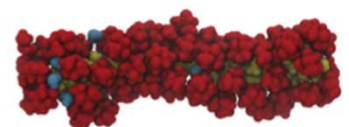
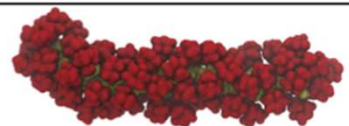


Rabideau, B.D. Ismail, A.E. *J. Phys. Chem. B* (2015), 119, 15014-15022



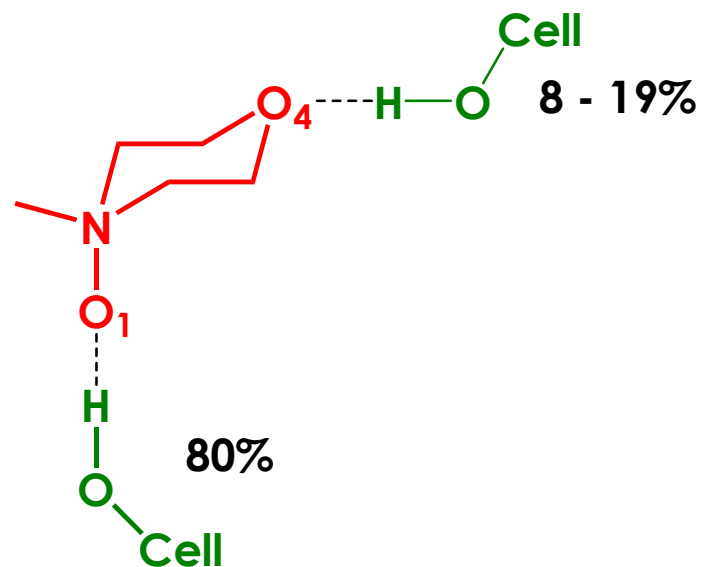
Surface

Coverage of the cellulose surface by NMMO: NMMO, Water, Cellulose



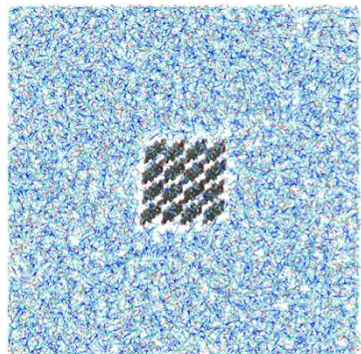
In the first solvation shell, O1(NMMO) is bound to OH-Cell.

Water within the first solvation shell will be located in gaps between these hydrophobic units.

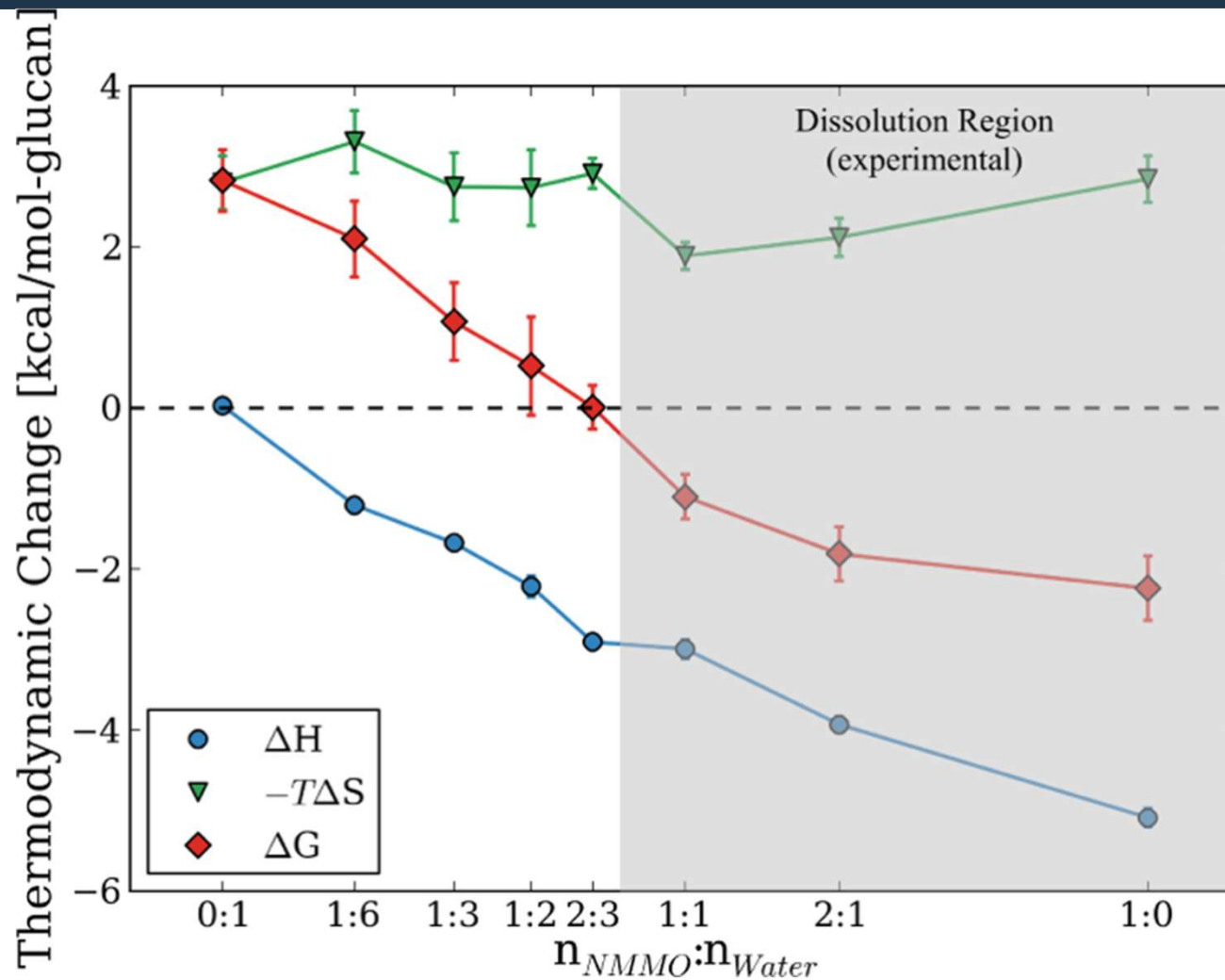
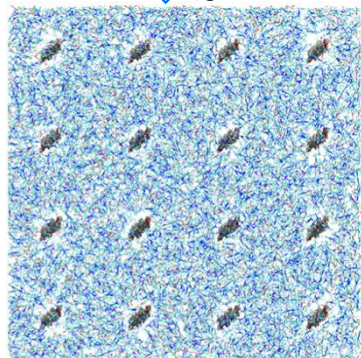


Thermodynamics of Cellulose Dissolution

15 wt% Cellulose

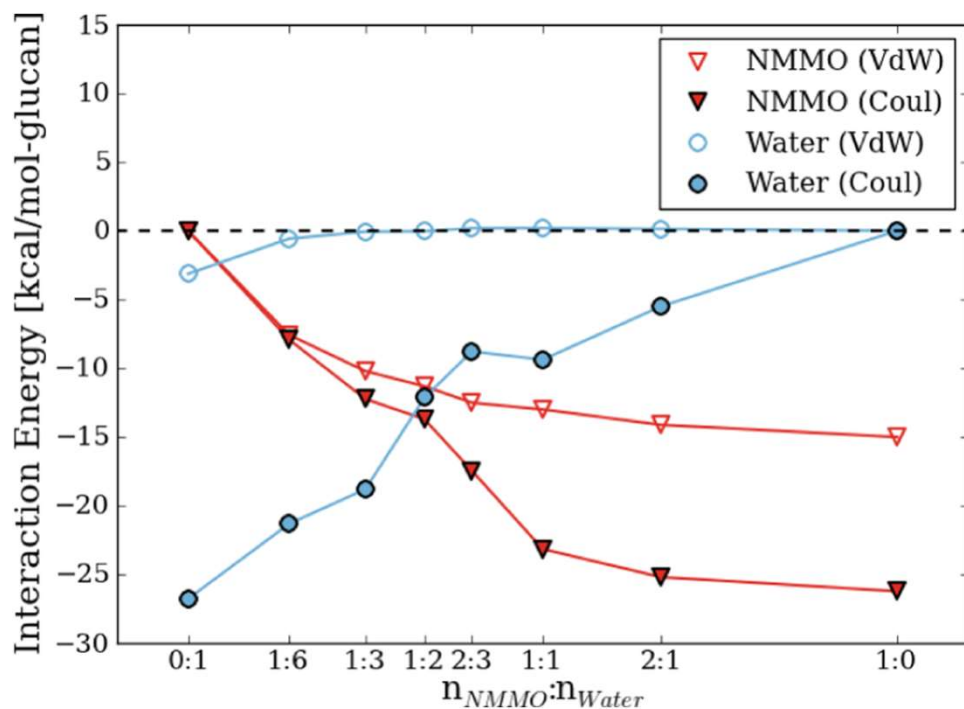


Dissociation



Two-phase thermodynamic method

Coulombic and VdW of NMMO and Water



At 1:1

- 50% Coulombic interaction from NMMO
- 30% vdW contribution from NMMO and
- 20% Coulombic interactions of water.

NMMO's nonpolar character allows cellulose to **recover most of the vdW's energy** that it loses during decrystallization.

Hydrophobic nature of the **solvent** tolerates the presence of water at low concentration