Conference or Workshop Item:

Ries, ME, Radhi, A, Keating, AS et al. (2 more authors) (2014) NMR relaxometry, diffusion, and rheology studies of carbohydrates in ionic liquids. In: 247th National Spring Meeting of the American-Chemical-Society (ACS), 16-20 Mar 2014, Dallas, TX.

NMR RELAXOMETRY, DIFFUSION AND RHEOLOGY STUDIES OF CARBOHYDRATES IN IONIC LIQUIDS

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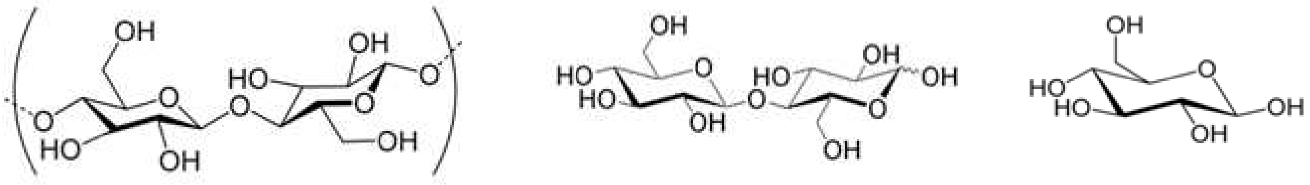
Tatiana Budtova: Centre de Mise en Forme des Materiaux, MINES Paris Tech, Sophia Antipolis, France.

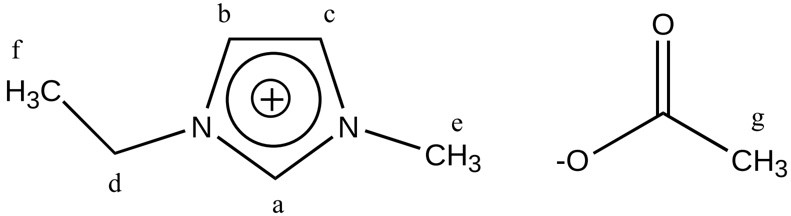
IL / CELLULOSE / CELLOBIOSE / GLUCOSE

System

- Avicel microcrystalline (DP=180) Cellulose $(C_6H_{10}O_5)_n$ / Cellobiose $(C_{12}H_{22}O_{11})$ / Glucose $(C_6H_{12}O_6)$;



- Ionic Liquid [C2mim][OAc] (EMIMAc), direct solvent for cellulose;



- 0%, 1%, 3%, 5%, 10% and 15% carbohydrate by weight,
  20 °C to 70 °C inclusive in steps of 10 °C.

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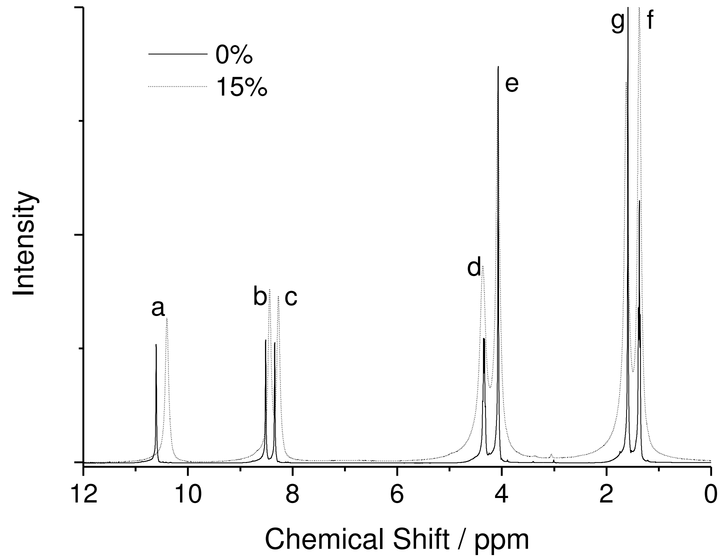
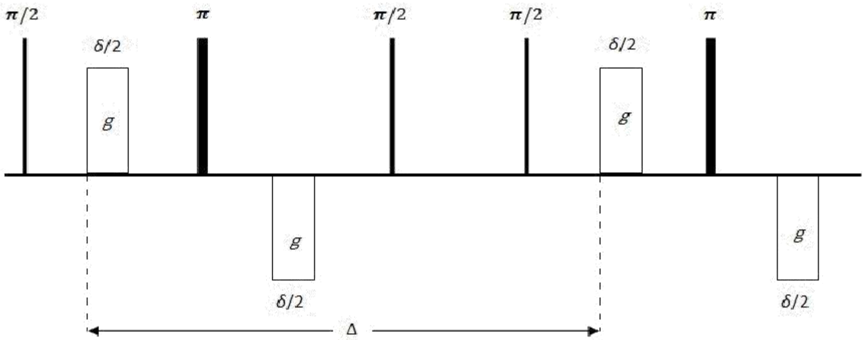
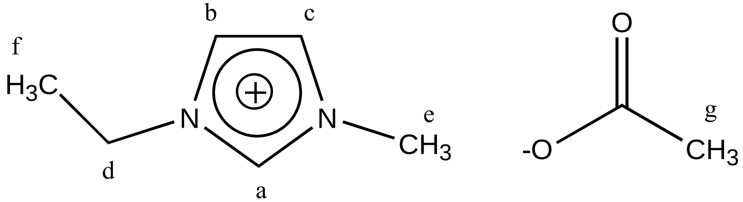
Techniques

- Diffusion measured by NMR stimulated echo pulse sequence with bipolar gradients.

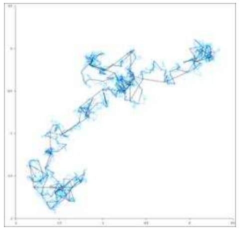
$$\ln\left(S_i / S_{i0}\right) = -D_i \gamma^2 g^2 \delta^2 \left(\Delta - \delta/3\right)$$

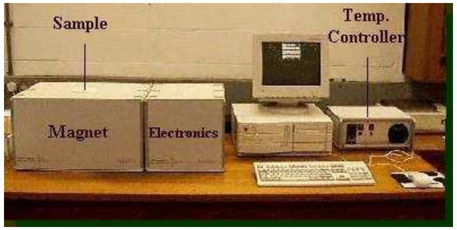






- Viscosity (zero shear rate)
- Low field (20 MHz) NMR Relaxometry
  Inversion Recovery
  CPMG spin echo sequence





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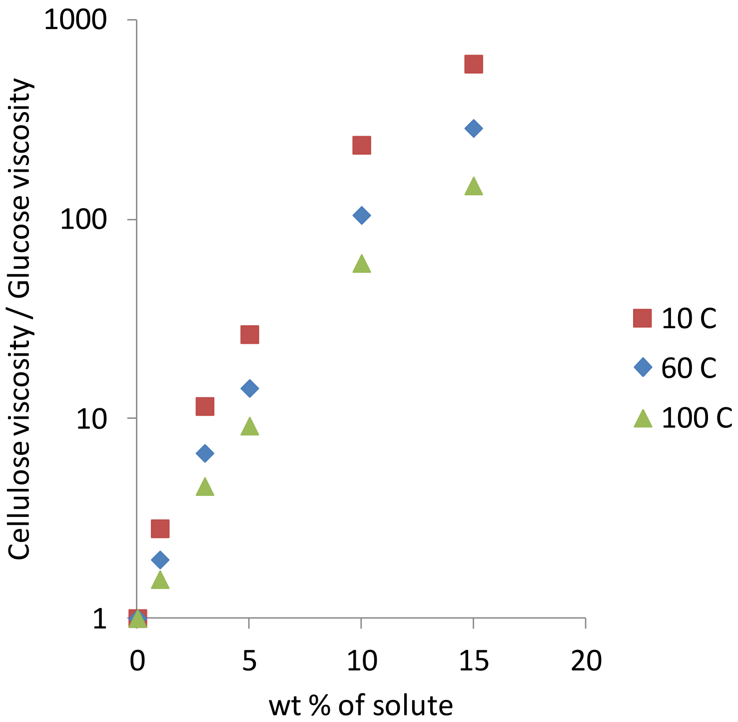
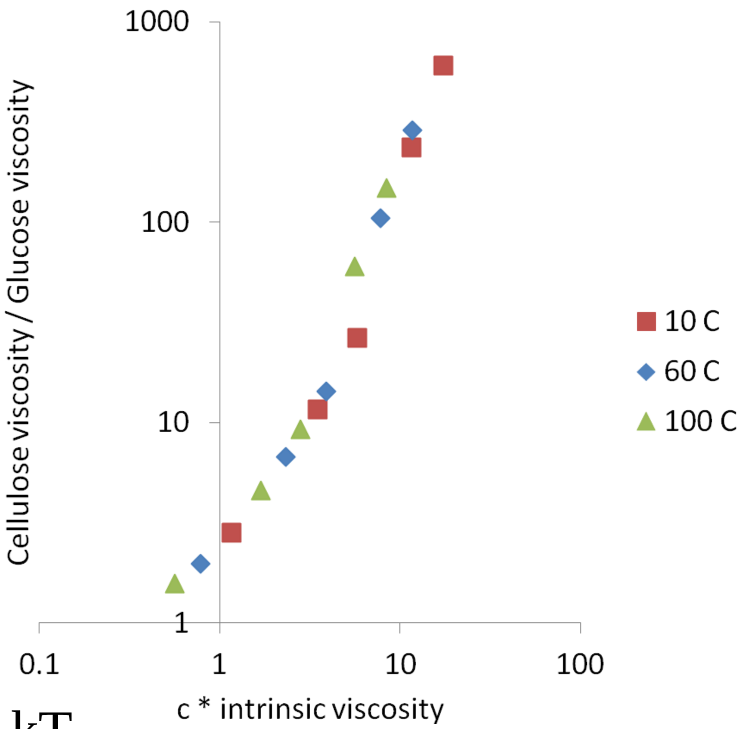
Viscosity

- The ratio for a given weight % of the viscosity of **cellobiose to glucose is 1.01 +/- 0.03**.
- The ratio for a given weight % of the viscosity of **cellulose to glucose:**





$$D_i(T) = \frac{1}{\eta} \frac{kT}{6\pi R_{H,i}}$$

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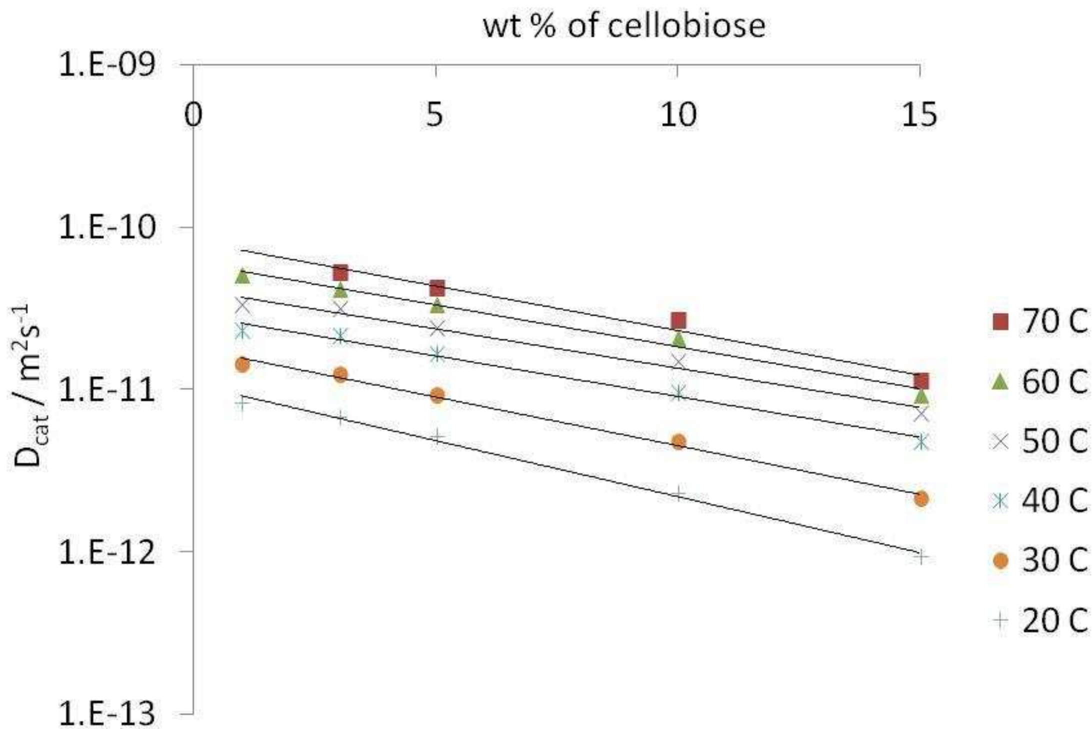
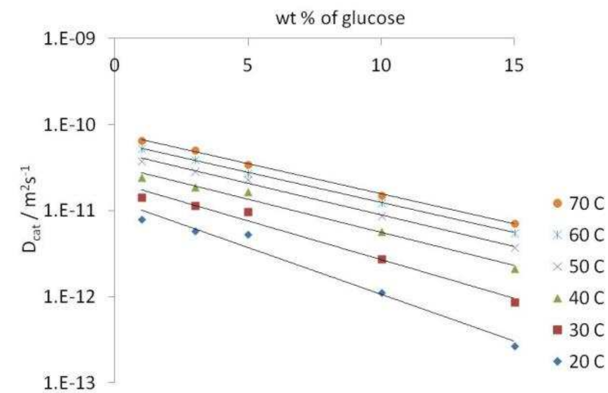
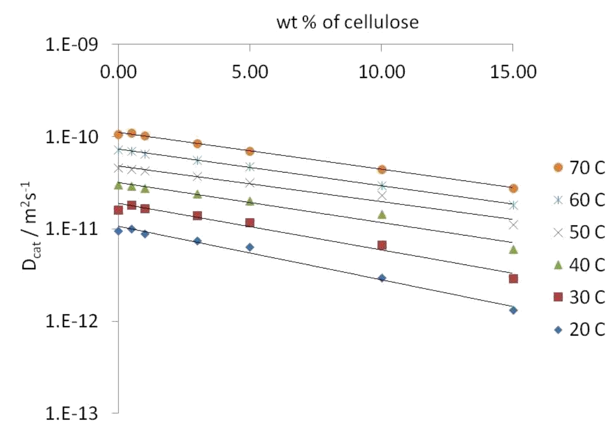
Diffusion

- Cation







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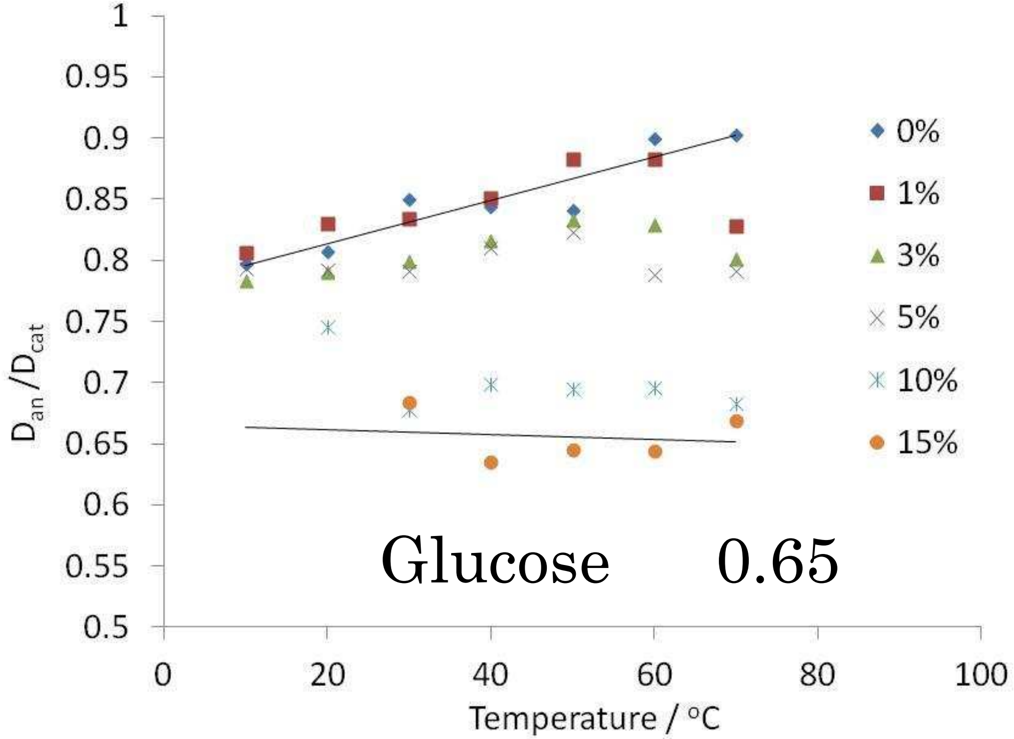
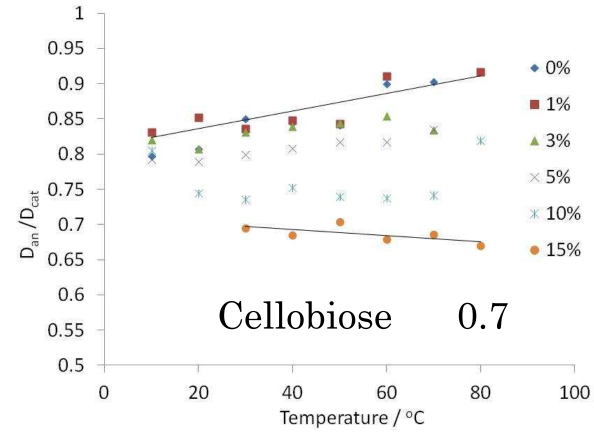
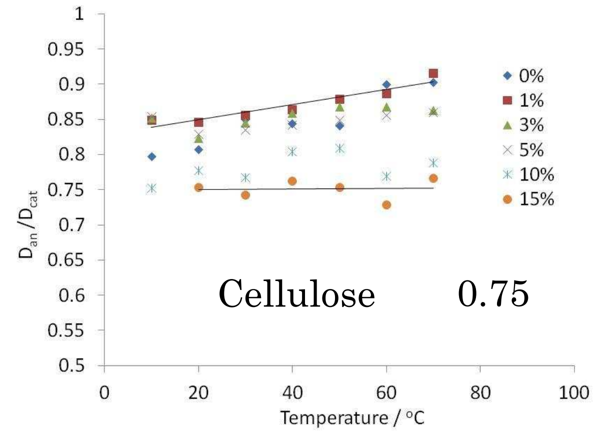
Diffusion

- Ratio anion / cation (anomalous)







$$D_i(T) = \frac{1}{\eta}\frac{kT}{6\pi R_{H,i}}$$

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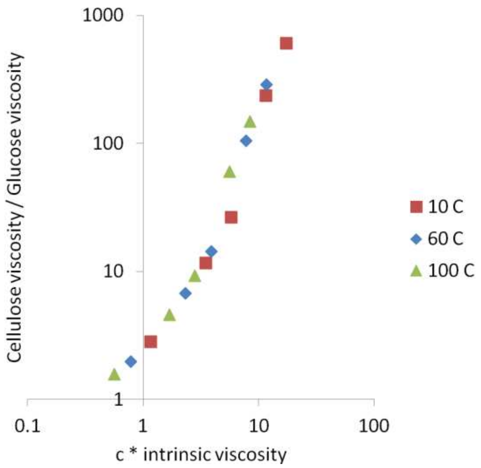
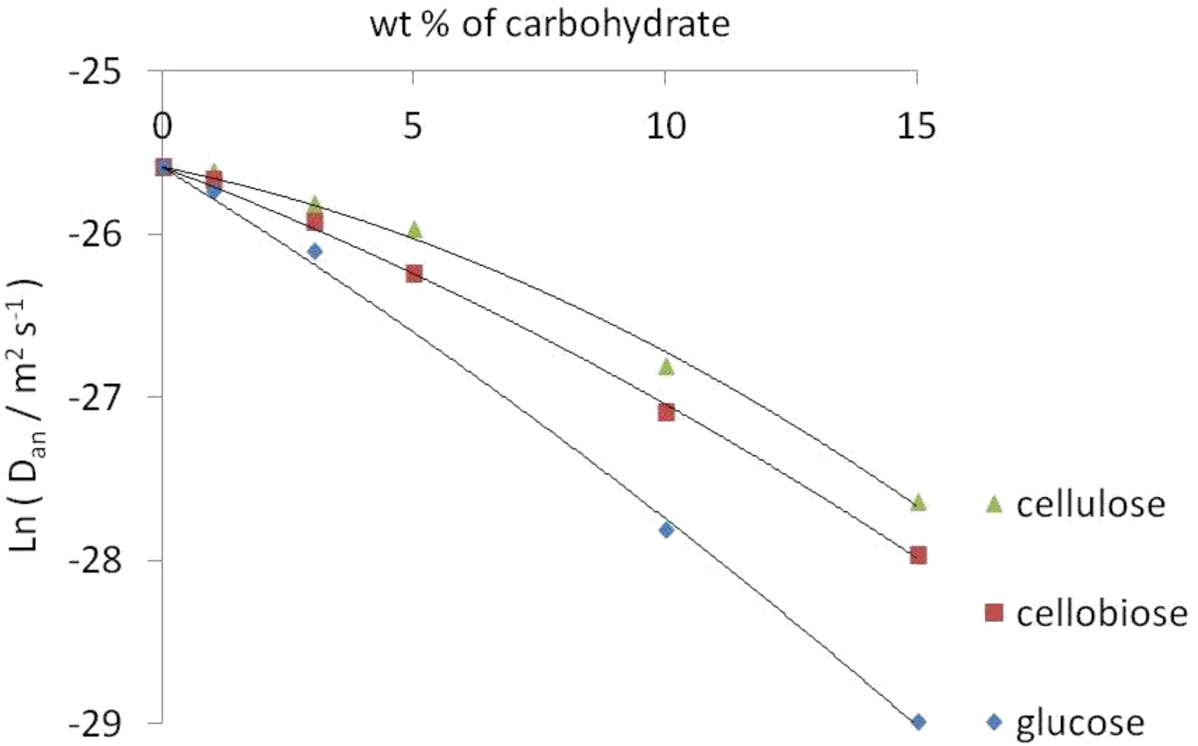
Diffusion vs viscosity

- Dependence on carbohydrate concentration.





$$D_i(T) = \frac{1}{\eta}\frac{kT}{6\pi R_{H,i}}$$

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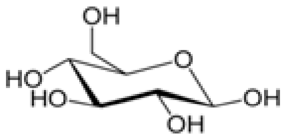
OH groups

- Glucose / Cellobiose / Cellulose;

5



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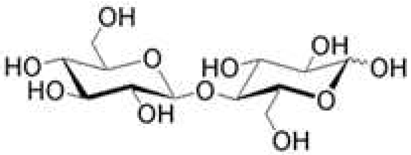

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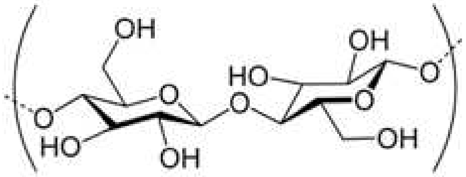

$$f = N \times \frac{M_{IL}}{M_{GU}} \times \frac{\phi}{100-\phi}$$

- Parameter *f* is the molar ratio of OH groups to IL molecules
Termed bound / associated fraction because it is proportional to the fraction of IL molecules involved in dissolving a glucose unit.

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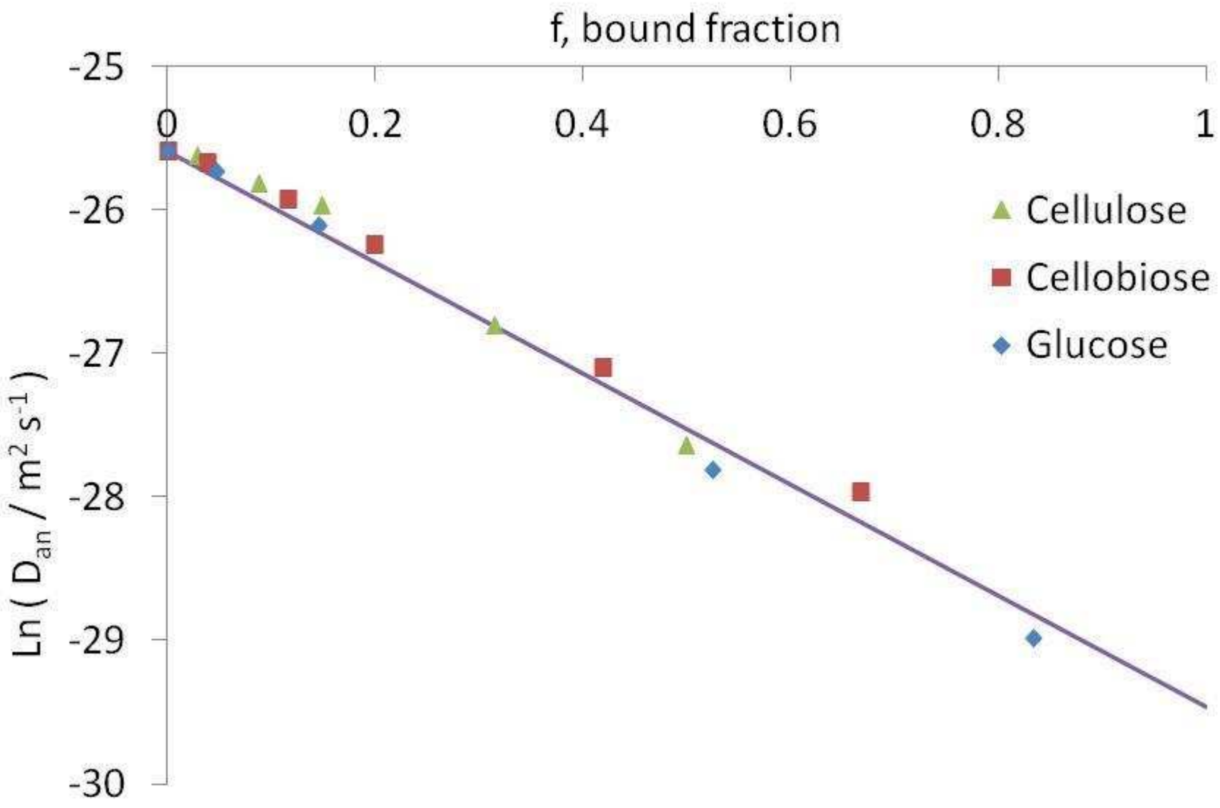
Diffusion

- Anion



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Viscosity and Diffusion of a mixture

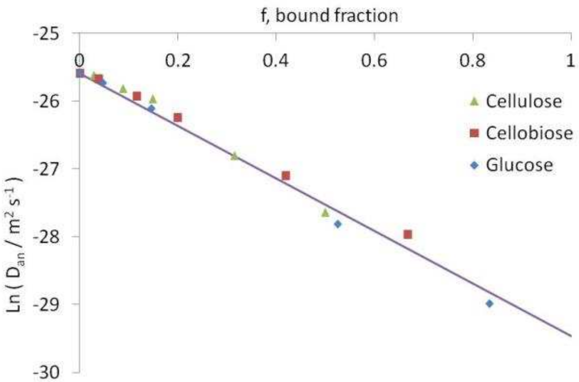
- Ideal Mixing

$$\ln\eta = x_1 \ln\eta_1 + x_2 \ln\eta_2$$

- Arrhenius law for mixing 1887, expressed in volume fraction
- Kendall showed in 1917 rule worked better with mole fraction
- Powell, Roseveare, Eyring in 1941 derived this for when excess free energy of mixing is zero

$$D_i(T) = \frac{1}{\eta}\frac{kT}{6\pi R_{H,i}}$$

$$\ln(D) = x_1 \ln D_1 + x_2 \ln D_2$$



- Free energy of activation is additive on mole fraction

$$E_A = (1-f)E_{free} + fE_{bound}$$

$$D = D_0 \exp\left(-\frac{E_A}{RT}\right)$$

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Diffusion of a mixture

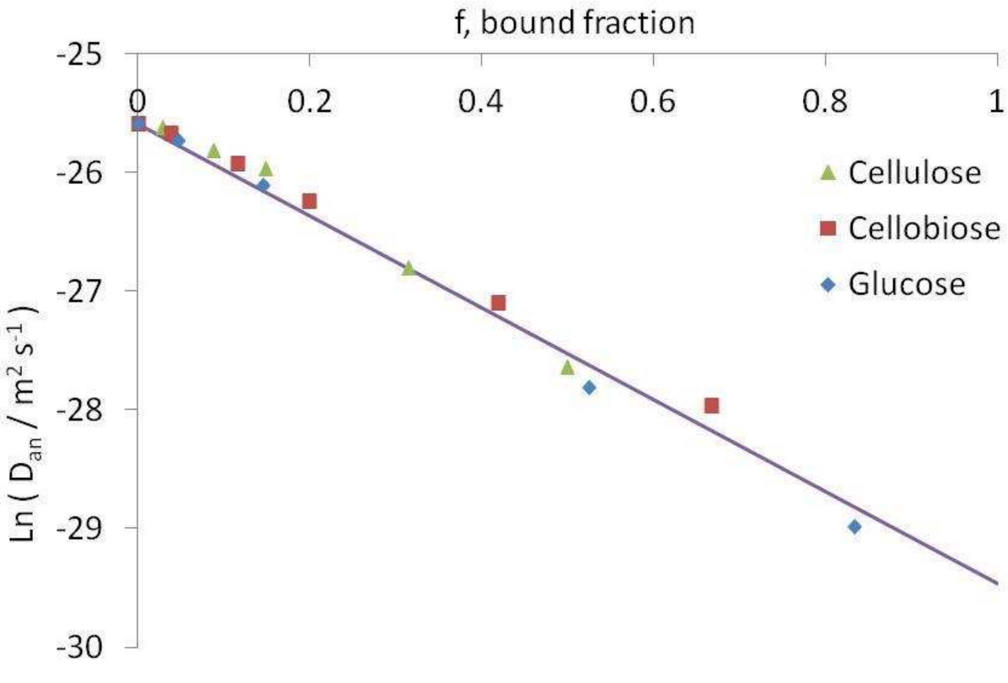
- Concentration dependence

$$E_A = (1 - f)E_{free} + fE_{bound}$$

$$D = D_0 \exp\left(-\frac{E_A}{RT}\right)$$

$$\ln D = \left(\ln D_0 - \frac{E_{free}}{RT}\right) - f \times \frac{\Delta E}{RT}$$

$$\Delta E = E_{bound} - E_{free}$$



- ΔE = 9.3 ±0.9 kJ/mol

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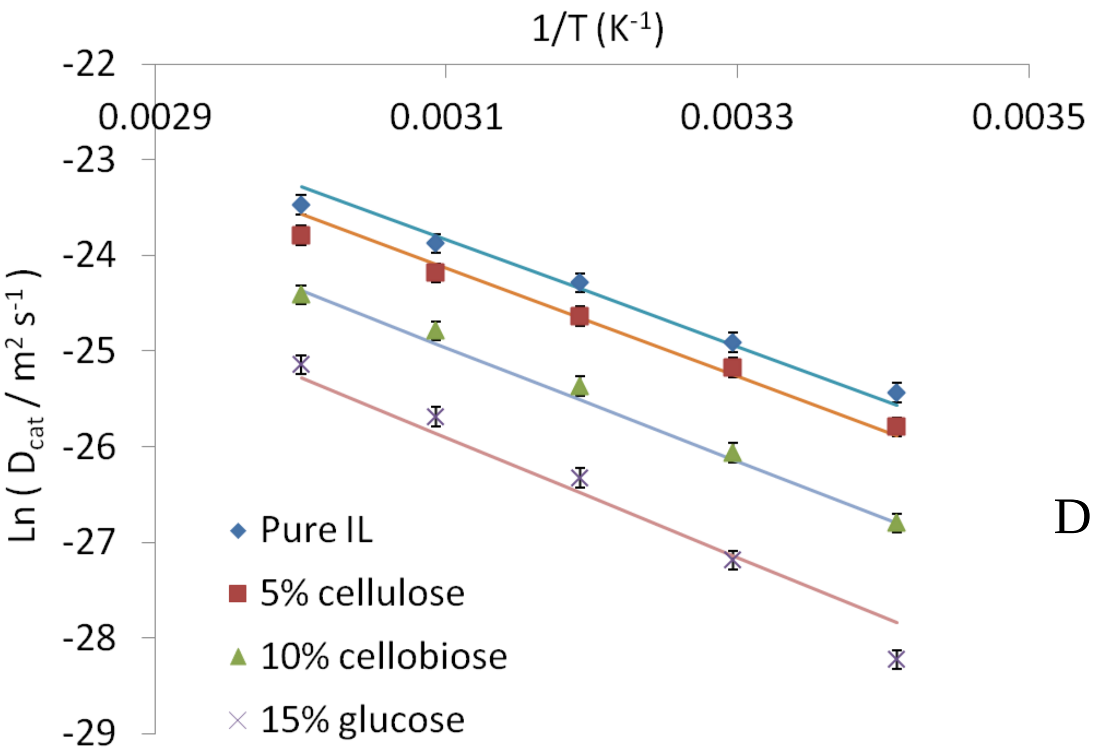
Diffusion temperature dependence

- Cation



$$D = D_0 \exp\left(-\frac{E_A}{RT}\right)$$

- D_0 for anion data 1.6 ±0.2 ×10^{-3} m^{2}s^{-1} and for the cation data 1.4 ±0.2 ×10^{-3} m^{2}s^{-1}.

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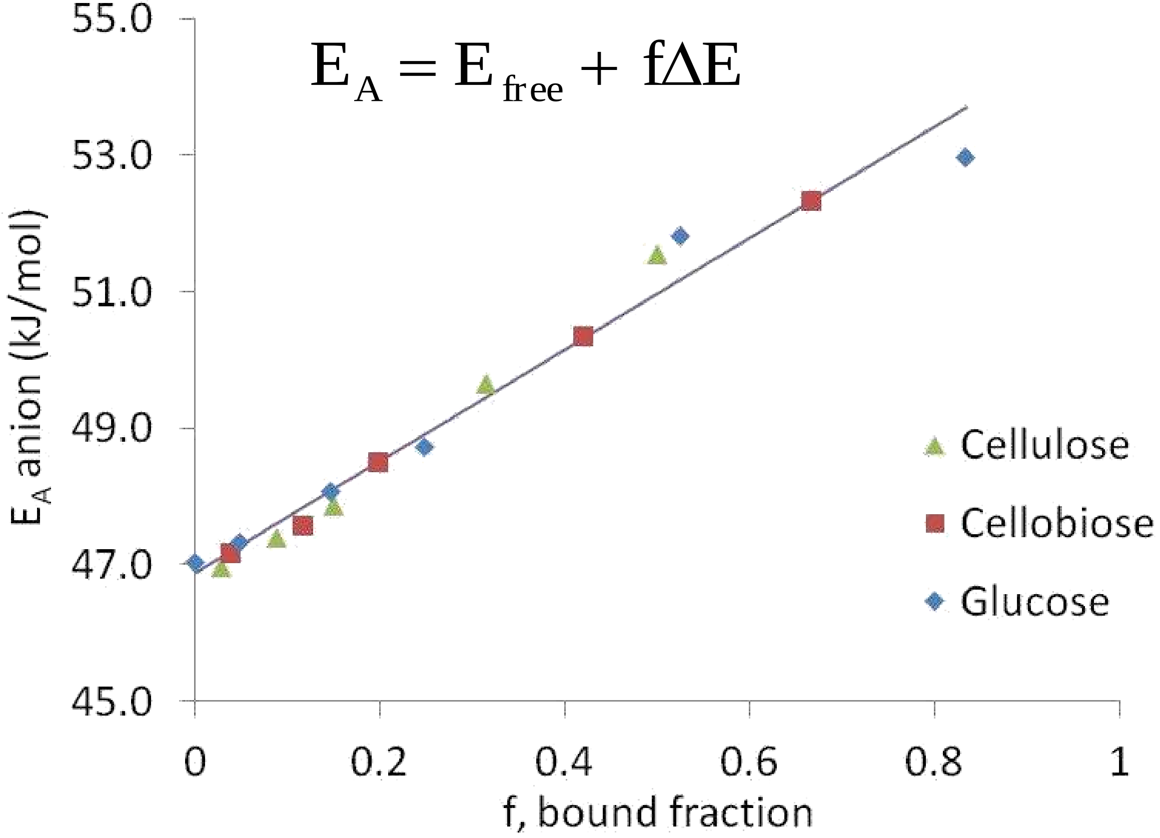
Activation Energy

- Anion



- Anion: $\Delta E = 8.2 \pm 0.4$ kJ/mol, Cation: $\Delta E = 7.6 \pm 0.4$ kJ/mol

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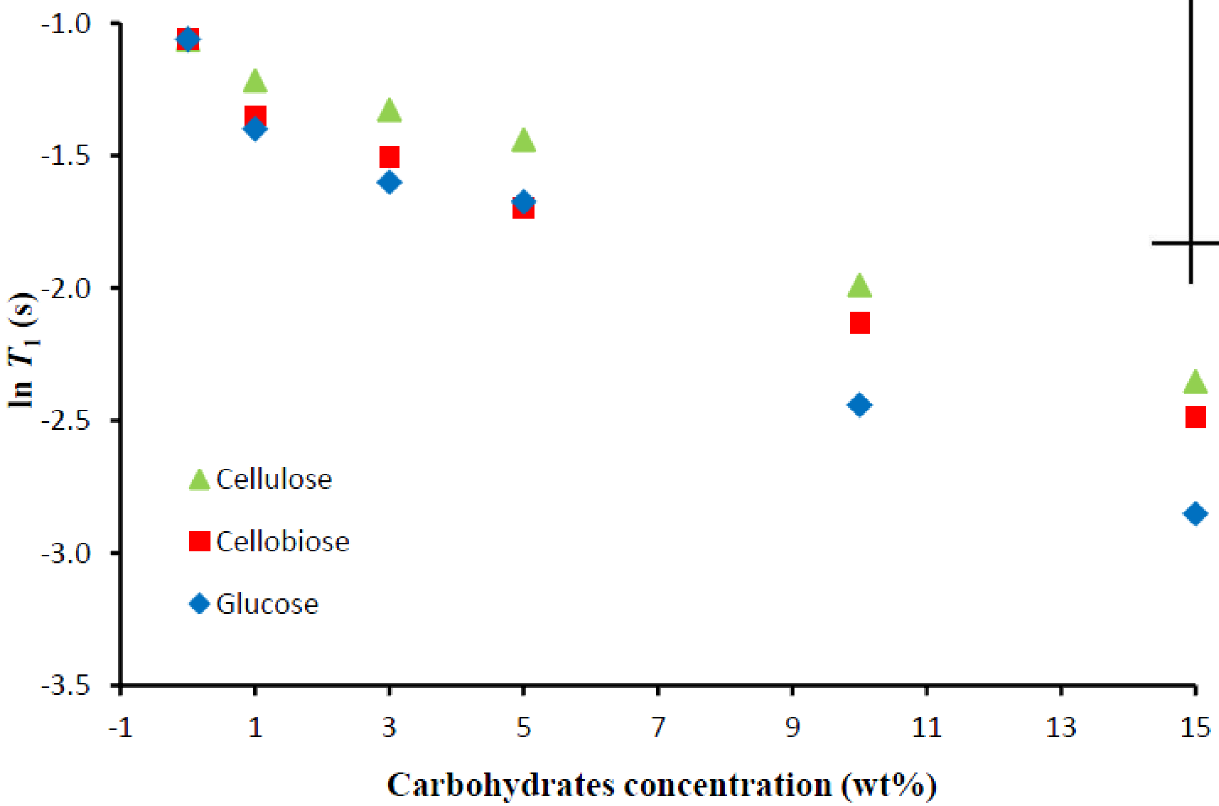
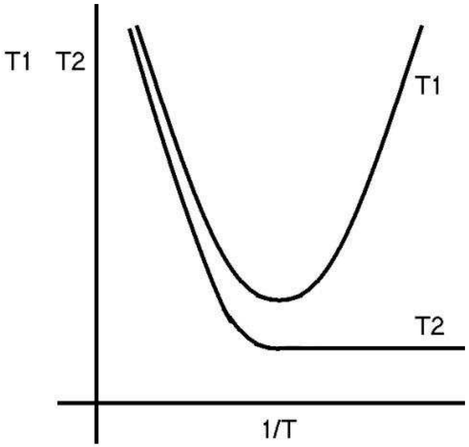
Low Field NMR Relaxometry

- T_1 longitudinal relaxation





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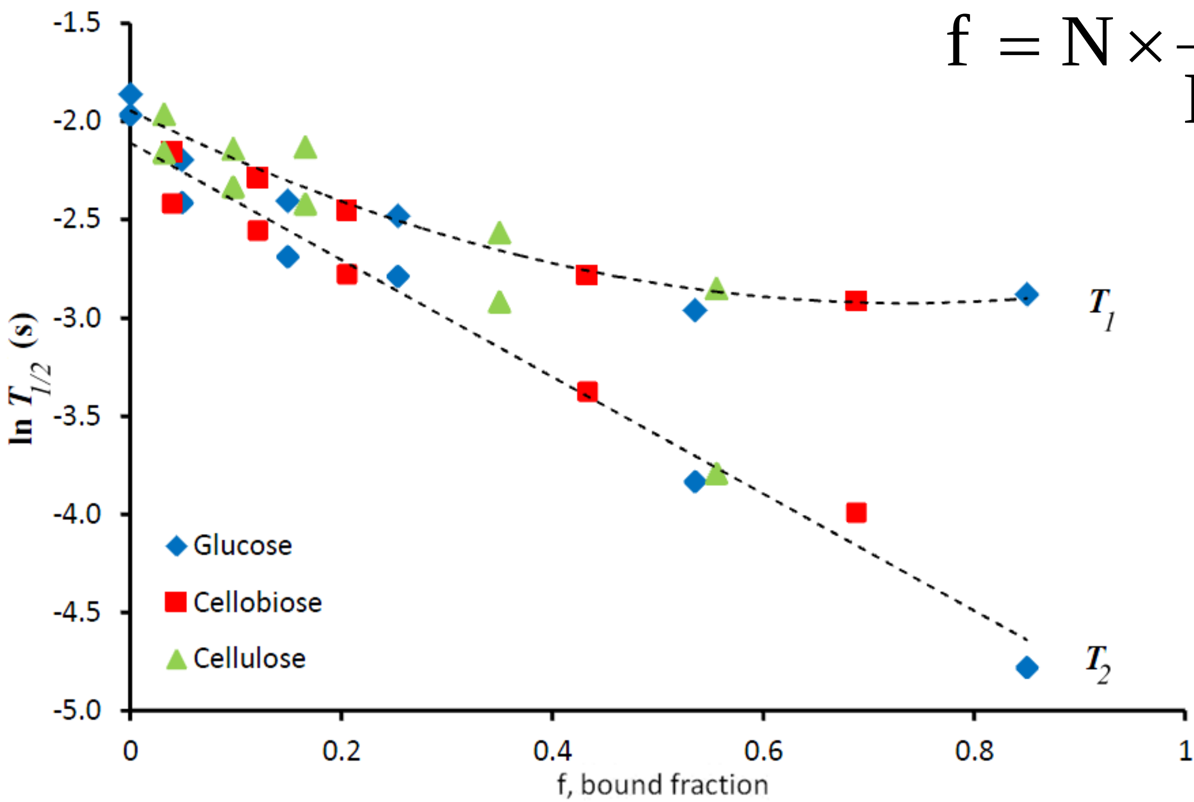
Low Field NMR Relaxometry

- T_1 longitudinal and T_2 transverse relaxation

$$f = N \times \frac{M_{IL}}{M_{GU}} \times \frac{\phi}{100 - \phi}$$



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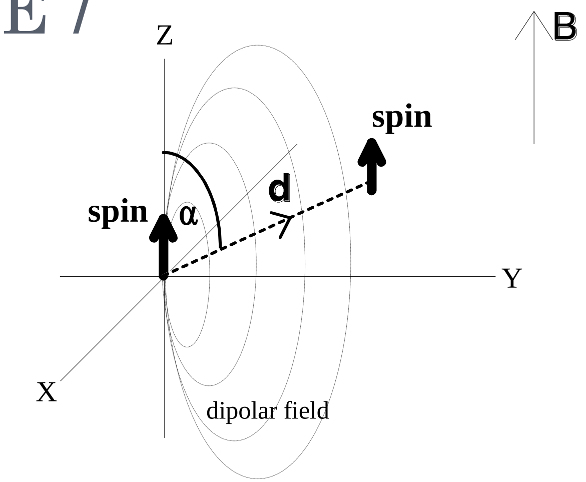
Low Field NMR Relaxometry

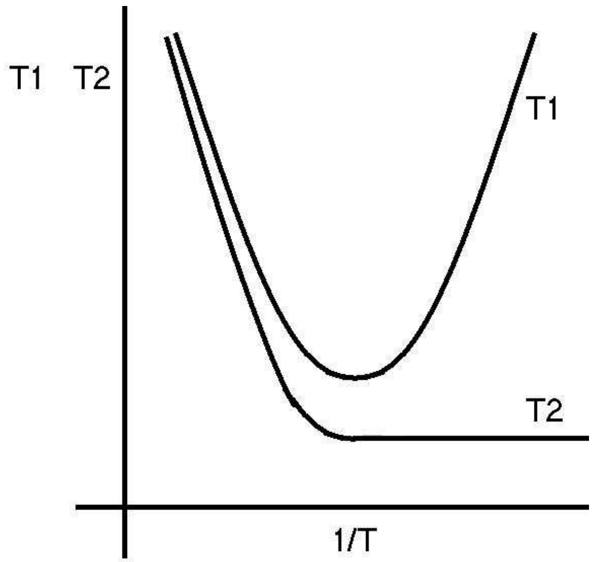
- *BPP analysis*

$$\frac{1}{T_1} = K\left(\frac{\tau_c}{1+\omega_o^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_o^2\tau_c^2}\right)$$

$$\frac{1}{T_2} = \frac{K}{2}\left[3\tau_c + \frac{5\tau_c}{1+\ \omega^2\ \tau_c^2} + \frac{2\tau_c}{1+4\omega^2\tau_c^2}\right]$$

$$\tau_c = \tau_o exp\left(\frac{E_a[\tau_c]}{k_B T}\right)$$





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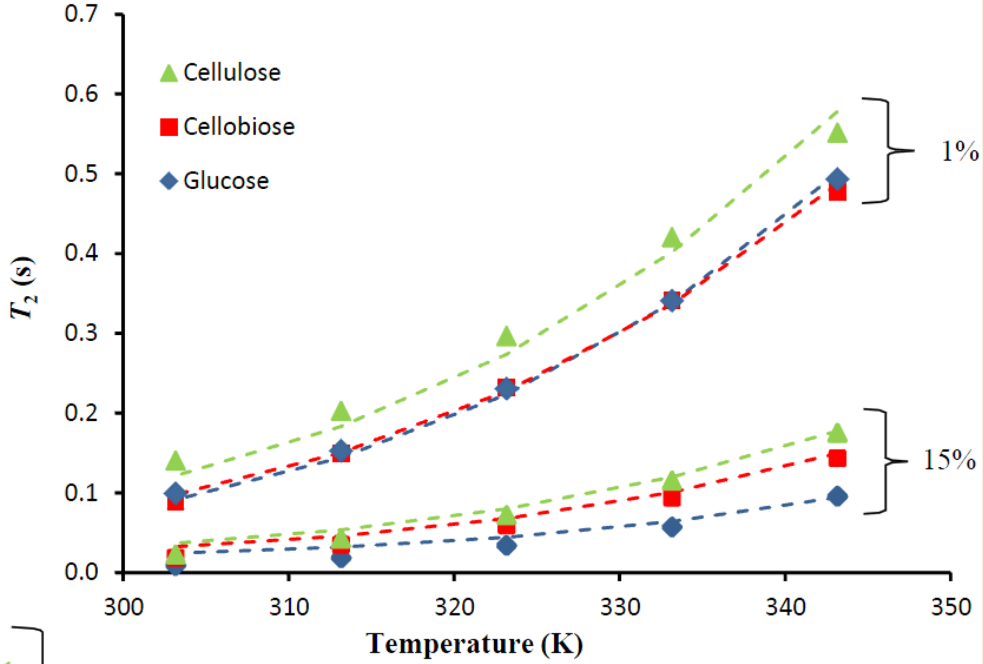
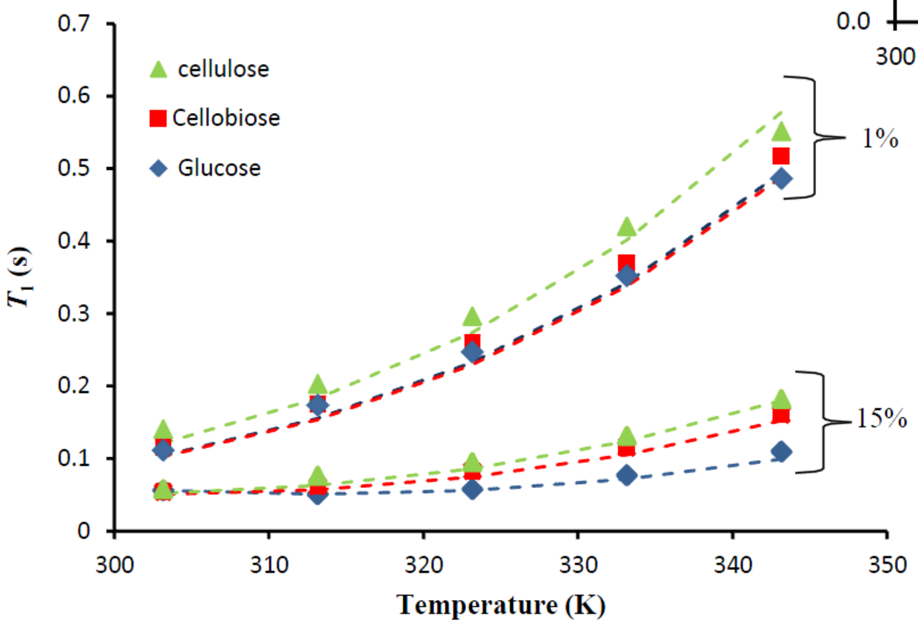
Low Field NMR Relaxometry

- *BPP analysis*
  $\tau_0 = 1.9\ 10^{-15}$ s
  $\tau_c \sim 10^{-10}$ s
  inter-proton distance = $2.2\ 10^{-10}$ m





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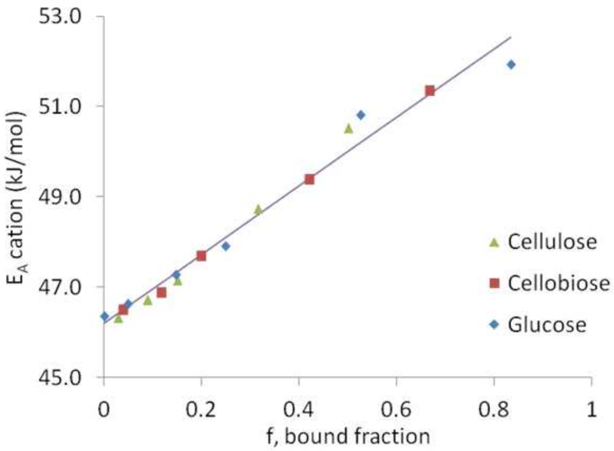
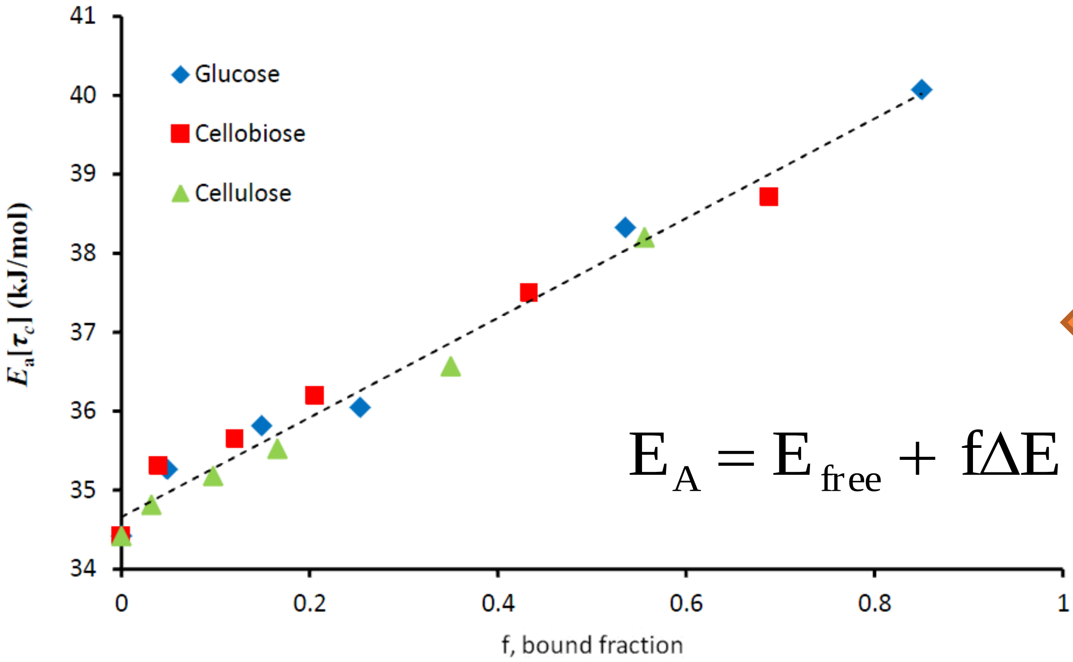
Low Field NMR Relaxometry

- *BPP analysis*
  $\tau_0 = 1.9\ 10^{-15}$ s
  $\tau_c \sim 10^{-10}$ s
  inter-proton distance = 2.2 10 $^{-10}$ *m*
  -12 kJ/mol

Diffusion





Relaxometry

$$E_A = E_{free} + f\Delta E$$

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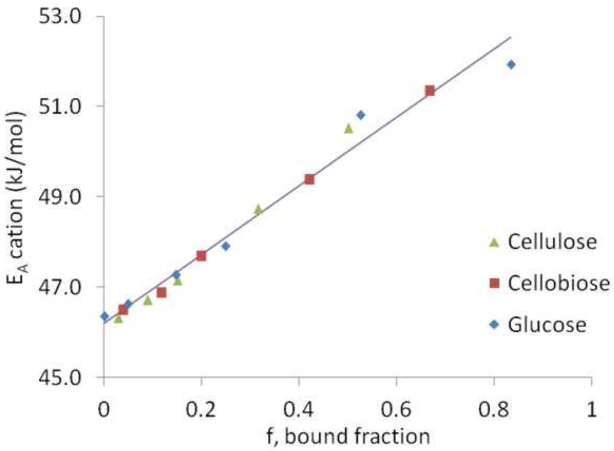
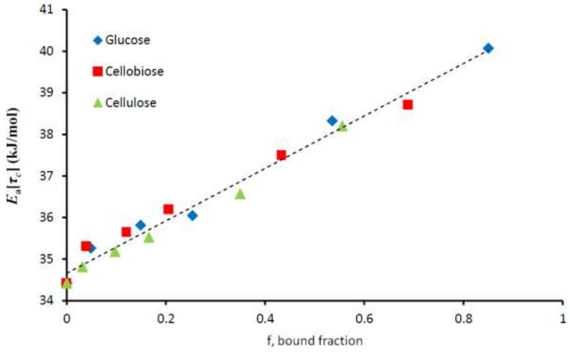


Low Field NMR Relaxometry

- *Stokes-Debye-Einstein*

$$\tau_{rot} = \frac{4\pi R_H^3 \eta}{3k_B T} \qquad \tau = \tau_0 \exp\left(\frac{E_A[rot]}{RT}\right)$$

- *Stokes-Einstein*



$$D = \frac{kT}{6\pi\eta R_H} \qquad D = D_0 \exp\left(-\frac{E_A[rot] + E_{hole}}{RT}\right)$$

- *DE O'Reilly 1968*

$$D = \frac{2}{9} R_H^2 \frac{1}{\tau_0} \exp\left(\frac{E_{hole}}{RT}\right)$$

- *Therefore can calculate: E_{hole} = 11 kJ/mol and we found 12 kJ/mol*

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Conclusions

- Diffusion of IL in Cellulose / Cellobiose / Glucose solutions;
- Cellulose the most effective at increasing the viscosity;
- Glucose most effective at slowing the ions down;
- Ratio of OH groups to IL molecules determines the diffusion of the ions;
- This can be thought of as an ideal mixing law, between bound and free ions;

- NMR relaxometry measured of IL in Cellulose / Cellobiose / Glucose solutions;
- Glucose the most effective in slowing down reorientation;
- Ratio of OH groups to IL molecules determines the NMR relaxometry;
- Agreement found between diffusion data and relaxometry data;
- Cost of creating a “whole” for diffusion about 12 kJ/mol.

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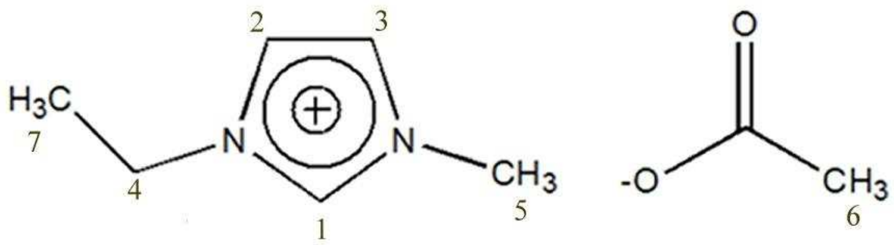
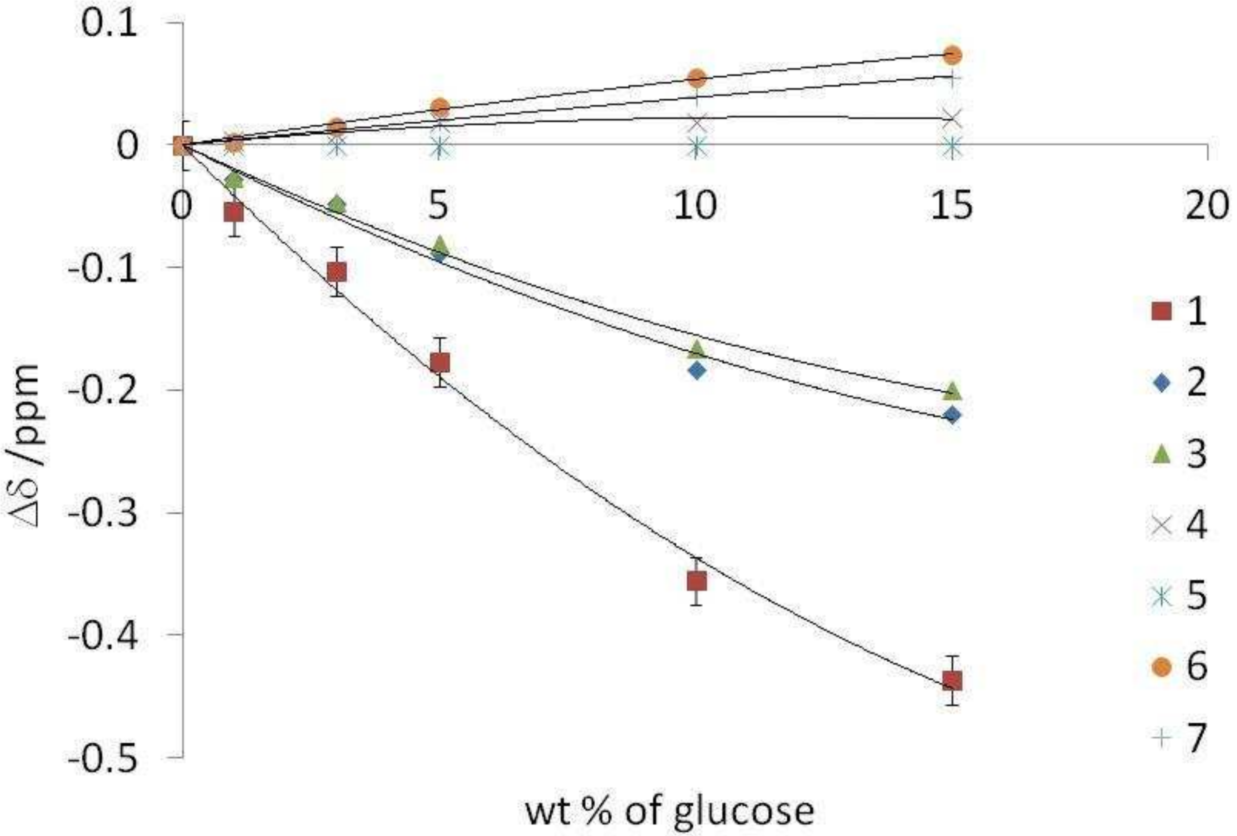


ppm

- Glucose



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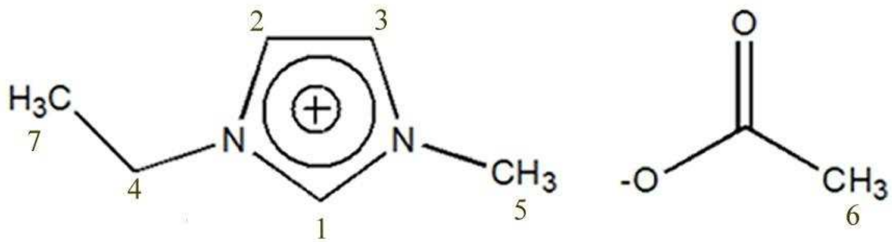
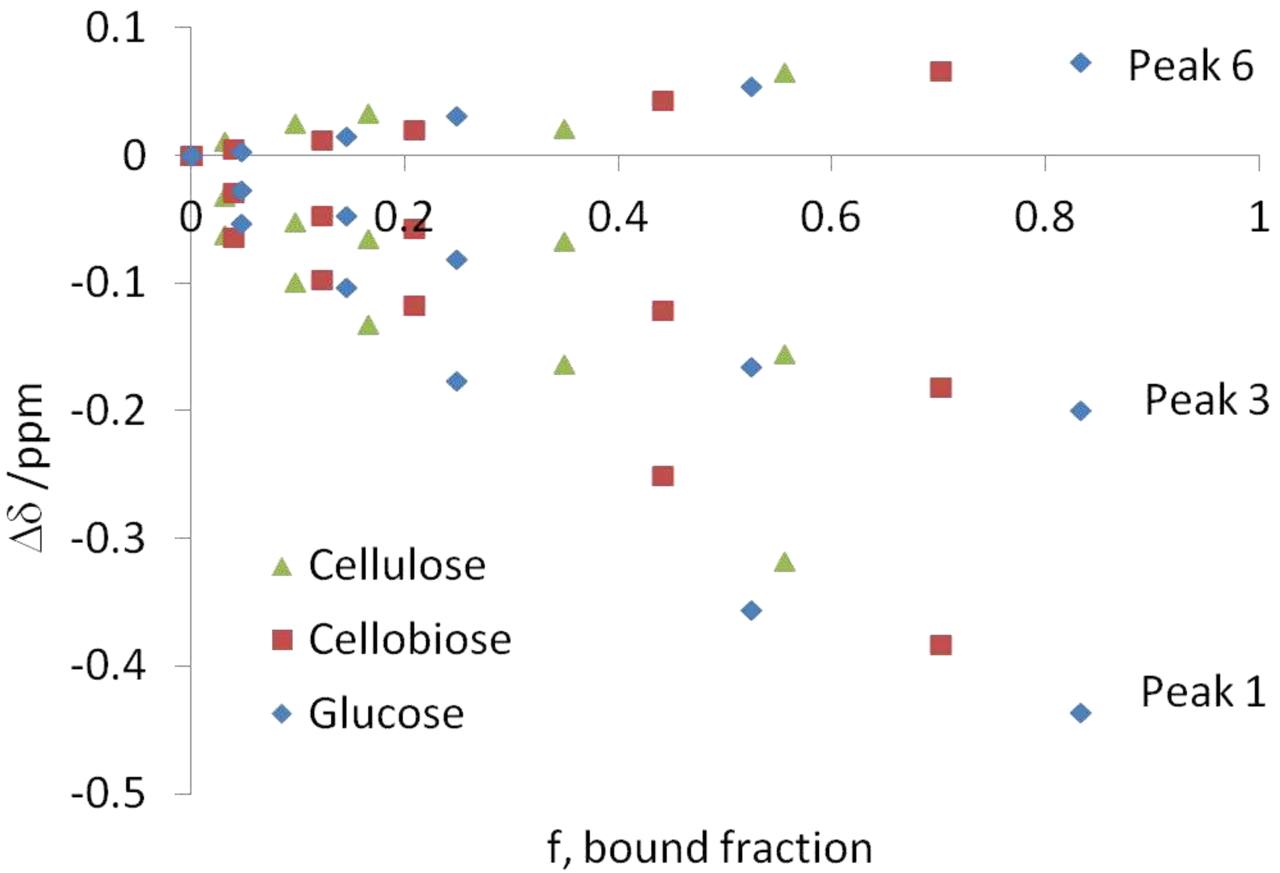


ppm

- Carbohydrate



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