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

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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.

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

- 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

![Graphs showing diffusion data for different wt % of cellubiose and glucose at various temperatures.](image)
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**Diffusion**
- Ratio anion / cation (anomalous)

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

- **Cellulose**: 0.75
- **Celllobiose**: 0.7
- **Glucose**: 0.65
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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;

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.

\[ f = \frac{N \times \frac{M_{IL}}{M_{GU}} \times \frac{\phi}{100 - \phi}} \]
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Diffusion
- Anion

\[
\text{Ln} \left( \frac{D_{an}}{m^2 \text{s}^{-1}} \right) \text{ vs. } f, \text{ bound fraction}
\]

- Cellulose
- Cellobiose
- Glucose
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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
  \[ E_A = (1 - f)E_{\text{free}} + fE_{\text{bound}} \]
  \[ D = D_0 \exp\left( -\frac{E_A}{RT} \right) \]
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Diffusion of a mixture

- Concentration dependence

\[ E_A = (1 - f)E_{\text{free}} + fE_{\text{bound}} \]

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

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

\[ \Delta E = E_{\text{bound}} - E_{\text{free}} \]

- \( \Delta E = 9.3 \pm 0.9 \text{ kJ/mol} \)
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Diffusion temperature dependence

- Cation

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

- \( D_0 \) for anion data \(1.6 \pm 0.2 \times 10^{-3} \text{ m}^2\text{s}^{-1}\) and for the cation data \(1.4 \pm 0.2 \times 10^{-3} \text{ m}^2\text{s}^{-1}\).
**Activation Energy**

- Anion:

  \[ E_A = E_{\text{free}} + f \Delta E \]

- Anion: \( \Delta E = 8.2 \pm 0.4 \text{ kJ/mol} \), Cation: \( \Delta E = 7.6 \pm 0.4 \text{ kJ/mol} \)
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Low Field NMR Relaxometry

- $T_1$ longitudinal relaxation

![Diagram showing $\ln T_1$ vs. carbohydrates concentration (wt%) with different symbols for Cellulose, Cellobiose, and Glucose, and a plot of $1/T$ vs. $T_1$ with curves for $T_1$ and $T_2$.]
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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

\[
\frac{1}{T_1} = K \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right)
\]

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

\[
\tau_c = \tau_0 \exp \left( \frac{E_a[\tau_c]}{k_B T} \right)
\]
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Low Field NMR Relaxometry

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

![Graphs showing T_1 and T_2 vs. temperature for cellulose, cellobiose, and glucose.](image)
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Low Field NMR Relaxometry

- **BPP analysis**
  \( \tau_0 = 1.9 \times 10^{-15} \text{ s} \)
  \( \tau_c \approx 10^{-10} \text{ s} \)
  inter-proton distance = \( 2.2 \times 10^{-10} \text{ m} \)
- \( -12 \text{ kJ/mol} \)

\[ E_A = E_{\text{free}} + f \Delta E \]
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Low Field NMR Relaxometry

- **Stokes-Debye-Einstein**
  \[
  \tau_{rot} = \frac{4\pi R_H^3 \eta}{3k_B T} \quad \tau = \tau_0 \exp\left(\frac{E_A[rot]}{RT}\right)
  \]

- **Stokes-Einstein**
  \[
  D = \frac{kT}{6\pi \eta R_H} \quad D = D_0 \exp\left(-\frac{E_A[rot]+E_{\text{hole}}}{RT}\right)
  \]

- **DE O'Reilly 1968**
  \[
  D = \frac{2}{9} R_H^2 \frac{1}{\tau_0} \exp\left(\frac{E_{\text{hole}}}{RT}\right)
  \]

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

![Graph showing δ/ppm vs wt % of glucose with different markers for different concentrations.](image-url)
IL / CELLULOSE / CELLOBIOSE / GLUCOSE

ppm
- Carbohydrate

![Chemical structures](image)

![Graph](image)