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Characterisation of Lactose in the Liquid and Solid State using Nuclear Magnetic Resonance and Other Methods

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

at

Massey University

Jim Hargreaves

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Abstract

The anomeric composition of lactose is studied using polarimetry, gas liquid chromatography and a variety of nuclear magnetic resonance (NMR) methods and the results compared. As a result reliable characterisation based on solution methods is obtained. The measurement of the spectrum of nuclear spin-lattice relaxation times ($T_1$) of lactose powders demonstrate significant differences between crystalline and amorphous species and between the different crystalline forms of lactose. These differences form the basis of a new characterisation methodology of powdered lactose where measurements are performed in the solid state. The use of linear multi-exponential curve fitting algorithms (NNLS and Contin) to deduce the "relaxation spectrum" from the multiexponential decay curve (obtained using a low-cost wideline NMR machine) allows for the reliable interpretation of noisy and drift-affected inversion recovery data. The absence of spin-diffusion between crystalline and amorphous species enables the determination of the relative weight fractions of several lactose species in a mixed powder sample with a simple correlation to the relative intensities of relaxation time components of the $T_1$ spectrum. The $T_1$ values of amorphous lactose are shown to be sensitive to moisture content and the glass transition process. The quantitative results gained from using the $T_1$ method to characterise lactose can be applied to improve the functionality of lactose and lactose-containing powders.
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Chapter 1.

\( S \) : magnitude of the reciprocal space vector \((S = 2\sin \theta/\lambda).\)

\( \lambda \) : wavelength of the X-rays.

\( I_{cr}(S) \) : coherent scattering intensity of the crystalline regions.

\( I(S) \) : coherent scattering intensity of the crystalline and amorphous regions.

\( \overline{f^2} \) : mean square amplitude of the atomic scattering factor.

\( D \) : disorder function.

\( k \) : disorder parameter.

\( X_{cr} \) : crystallinity of the material.

\( \Delta H_{cr} \) : crystallisation enthalpy.

Chapter 3.

\( L \) : length of the polarimeter tube in decimeters.

\( c \) : anhydrous concentration of lactose in g/100 ml.

\( R_t \) : polarimeter reading at time \( t \).

\( R_e \) : polarimeter reading at equilibrium.

\([R]\) : the specific optical rotation.

\( w_\infty \) : weight of lactose sample used to determine \( R_e \).

\( W_a \) : anhydrous weight fraction.

\( \alpha \) : percentage of alpha lactose present in the sample.

\([\alpha]\) : specific optical rotation of alpha lactose.

\([\beta]\) : specific optical rotation of alpha lactose.

\( R_i \) : normalised optical rotation reading.

\( E_a \) : activation energy.

\( R \) : universal gas constant.

\( T \) : temperature (in Kelvin).

\( A \) : pre-exponential factor.

Chapter 4.

\( H \) : Zeeman Hamiltonian operator.

\( \gamma \) : gyromagnetic ratio.

\( \hbar \) : Plank's constant \((\hbar)/2\pi\).
**List of Symbols**

\(B_0\) : polarising magnetic field.

\(I_{x,y,z}\) : angular momentum operator.

\(B_1\) : oscillating magnetic field.

\(\omega\) : frequency.

\(U(t)\) : evolution operator.

\(H_{\text{rot}}\) : Hamiltonian operator in the rotating frame.

\(M_{x,y,z}\) : components of the spin magnetisation vector, \(M\).

\(M_0\) : magnitude of \(M_x(t)\) as \(t \to \infty\).

\(T_1\) : spin lattice relaxation time.

\(T_2\) : spin spin relaxation time.

\(\mu_0\) : permeability of free space.

\(I\) : vector operator representing angular momentum.

\(r_{ij}\) : internuclear vector.

\(r_{ij}\) : magnitude of the internuclear vector.

\(H_D\) : dipolar Hamiltonian operator.

\(W_{nn}\) : transition rate.

\(E_{n,m}\) : energies of states \(n\) and \(m\).

\(i\) : \(\sqrt{-1}\).

\(\tau_c\) : average correlation time.

\(J^{(s)}(\omega)\) : spectral density function.

\(\rho^*(t)\) : density operator in the rotating frame.

\(H_D^*(t)\) : dipolar Hamiltonian operator in the rotating frame.

\(\omega_0\) : Larmor frequency.

\(M(t)\) : equal to \(M_x(t)\)

\(A_i\) : amplitude of component \(i\).

\(y(t_i)\) : amplitude of multiexponential relaxation function at time \(t_i\).

\(s(T)\) : unknown amplitude of relaxation time \(T\).

\(t_i\) : time.

\(\chi^2\) : error function.

\(y_i\) : equal to \(y(t_i)\).

\(\gamma_i\) : datum point.

\(\sigma_i\) : variance of datum points \(y_i\).

\(x_m\) : column vector representing the true solution.

\(x\) : column vector of the current estimate to \(x_m\).

\(x_{i,j}\) : components of the column vector \(x\).

\(A\) : Hessian matrix.

\(b\) : gradient vector.

\(a\) : finite step required to find the minimum \((a = x - x_m)\).
List of Symbols

\( a_{ij} \) : components of vector \( a \).
\( \beta_i \) : first partial derivative of \( \chi^2 \) with respect to \( x \).
\( \alpha_{ij} \) : second partial derivative of \( \chi^2 \) with respect to \( x \).
\( x_{\text{next}} \) : next estimate of \( x \).
\( \lambda \) : constant.
\( s_j \) : spectral amplitude of component \( j \).
\( T_j \) : relaxation time component \( j \).
\( Q \) : Householder transformation matrix.
\( R_k \) : upper triangular matrix.
\( \mathbf{u} \) : an \( m \) vector.
\( \mathbf{u}^T \) : transpose of \( \mathbf{u} \).
\( \mu \) : constant.
\( H \) : matrix representing additional constraints used in continuum formulation.
\( \mathbf{c} \) : an \( n \) vector.
\( M'(t) \) : corrected magnetisation.

Chapter 6.

\( C_p \) : heat capacity at constant pressure.
\( \alpha_p \) : volume expansivity at constant pressure.
\( H \) : enthalpy.
\( V \) : volume.
\( p \) : pressure.
\( z \) : order parameter.
\( w_{1,2} \) : weight fraction of components 1 and 2.
\( T_g \) : glass transition temperature.
\( k \) : constant.
\( T_l \) : spin lattice relaxation time.
\( \mu_0 \) : permeability of free space.
\( \gamma \) : gyromagnetic ratio.
\( \hbar \) : Planck's constant \( \hbar/2\pi \).
\( r_{ij} \) : average intermolecular distance.
\( I \) : angular momentum operator.
\( \tau_c \) : average correlation time.
\( \omega \) : frequency.
\( \tau(T) \) : mechanical and electrical relaxation time at temperature \( T \).
\( C_{i,2}^* \) : arbitrary constants.
List of Symbols

\( T_g \): glass transition temperature.

\( \phi_{CR, t} \): relaxation times of crystallisation at temperatures \( T \) and \( T_g \) respectively.

Chapter 7.

\( M(t) \): amplitude of the inversion recovery signal at time \( t \).

\( M_0 \): amplitude of the inversion recovery signal at \( t = 0 \).

\( A_{am, cr} \): relative amplitude of the amorphous and crystalline parts of the inversion recovery signal respectively.

\( T_{ICR} \): spin lattice relaxation time of the crystalline part of the sample.