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Fitting of the beat pattern observed in NMR free-induction decay signals of concentrated carbohydrate–water solutions

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Abstract

A series of mathematical functions has been used to fit the proton free-induction decays (FIDs) of concentrated carbohydrate–water samples. For the solid protons, these functions included a sinc function, as well as the Fourier transforms of single and multiple Pake functions multiplied by a Gaussian broadening. The NMR signal from the mobile protons is described by an exponential function. It is found that in most cases the sinc function gives a satisfactory result and provides valuable information about the second moment M_2 and the ratio of solid to mobile protons (f_s/f_m). A good indication for using the sinc function is the presence of a beat in the FID. For high temperatures this approach breaks down, and a biexponential fit is more appropriate. If a clear dipolar splitting is observable in the NMR spectra, the Pake function (or a multiple Pake fit) should be used. In this case information about M_2 and f_s/f_m can also be obtained.
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1. Introduction

In many nuclear magnetic resonance (NMR) experiments on inorganic crystals and glasses [1,2], a small beat or oscillation is observed in the free-induction decay (FID). This beat is also observed in the FID of dry food materials [3], such as breakfast cereals, carbohydrate glasses [4–8], and pollen and seeds [9]. The origin of the beat arises from the residual local order within the sample, manifest by regular spacings between near neighbour protons, giving rise to a dipolar spectral line shape, also referred to as the "Pake pattern" [10–13]. As the short-range organisation of molecules in an amorphous system, and certainly that of the atoms within a molecule, can never be completely random, the observation of residual dipolar effects is not surprising.

In recent years, there has been an increasing interest in the use of solid-state low-resolution ^{1}H NMR spectroscopy to study low-water content food and biological materials, to provide information about the molecular motions and state of water in relation to the macroscopic material properties (i.e., stability) in the food industry [14] and seed preservation [9]. In a solid, the ^{1}H NMR spectrum and thus the FID are determined by magnetic dipolar interactions and are dependent upon the location of protons within the sample. Even in the simplest cases a rigorous derivation of the NMR spectrum of such a homonuclear system is extremely difficult. In addition, the mobile protons in the sample will contribute to the NMR spectrum, giving rise to an additional complexity. Therefore a simplified procedure to analyse FIDs containing a beat pattern would be useful. In the present work, we have examined a series of freeze-concentrated carbohydrate–water glasses and carried out a comparison between the various equations used to analyse the FIDs in order to assess the most suitable way to analyse the data.

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2. Theory

In a high magnetic field, and taking into account all pairs of proton spins, the spin Hamiltonian H_{DD} for homonuclear dipole–dipole coupling for the whole sample is given by [11,13]

$$H_{DD} = \sum_{i<j} b_{ij} \frac{1}{2} \left(1 - 3\cos^2 \theta_{ij}\right) \left(3I_{iz}I_{jz} - \mathbf{I}_i \cdot \mathbf{I}_j\right), \qquad (1)$$

where θ_{ij} is the angle between the vector joining the spins and the direction of the external magnetic field and $\mathbf{I}$ indicates the spin angular momentum and b_{ij} is given by

$$b_{ij} = \left(\frac{\mu_0}{4\pi}\right) \frac{\gamma_H^2 \hbar}{r_{ij}^3}. \qquad (2)$$

Here γ_H is the magnetogyric ratio of the proton and r_{ij} is the internuclear separation.

A generalised rigorous analysis of such a problem is not possible. Therefore, we will consider two approximations. The first approach is based on the assumption that nearest neighbour dipolar interactions dominate the NMR spectrum. This then gives rise to the Pake doublet line shape [12]. The second is related to a series expansion of the FID in terms of moments of the line shape. These two approaches are schematically illustrated in Fig. 1.

2.1. Pake doublet line shape approach

As there is a random orientation of the nuclei in the solid sample, the resulting NMR spectrum is a powder spectrum. The inverse cube dependence of r_{ij} in Eq. (2)
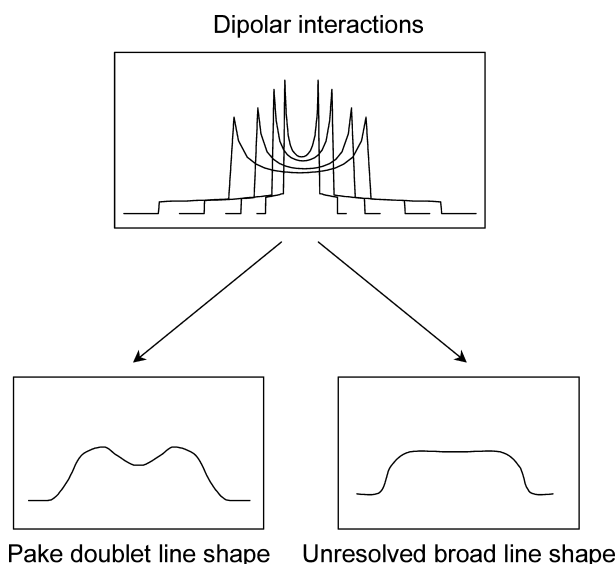

Fig. 1. Schematic illustration of the formation of a Pake doublet line shape or an unresolved line shape arising from nuclear dipole–dipole interactions. For simplicity it is assumed here that the dipolar line shape is a superposition of several Pake doublet spectra arising from pairs of nuclear spins. In reality the line shape is the complex result of a multi-interacting spin system, as given by Eq. (1).

implies that the nearest neighbours have the dominant influence in determining the dipolar interactions. This suggests a model where the NMR spectrum is considered to result from the nearest neighbour interactions, broadened by dipolar interactions from more distant nuclei to give a convoluted function. The nearest neighbour interaction can be treated with some rigour, whilst a Gaussian broadening represents that of the more distant neighbours.

For two proton spins at a distance r, the powder NMR spectrum corresponds to the Pake doublet line shape [10]. Such a spectrum $G_P(\omega)$ consists of the sum of two terms $G_1(\omega)$ and $G_2(\omega)$, one corresponding to each spin state of the neighbour:

$$G_P(\omega) = G_1(\omega) + G_2(\omega) \qquad (3)$$

with

$$G_1(\omega) = \left(\tfrac{1}{2}L + \omega\right)^{-\frac{1}{2}} \text{ in the range } -\tfrac{1}{2}L < \omega < L$$

and $G_1(\omega) = 0$ elsewhere,

and

$$G_2(\omega) = \left(\tfrac{1}{2}L - \omega\right)^{-\frac{1}{2}} \text{ in the range } -L < \omega < \tfrac{1}{2}L$$

and $G_2(\omega) = 0$ elsewhere.

In these equations, L is the maximum splitting generated by the nearest neighbour. Parameter L follows form Eq. (2)

$$L = \left(\frac{\mu_0}{4\pi}\right) \frac{\gamma_H^2 \hbar}{r^3}. \qquad (4)$$

The index P refers to the Pake doublet line shape.

The FID can be calculated through a Fourier transformation of the line shape function. Taking into account an additional broadening by distant nuclei, the FID for the Pake doublet case takes the form:

$$F_P(t) = \exp\left(-\frac{1}{2}a^2 t^2\right) \int_0^\infty G_P(\omega) \exp(-i\omega t)\, d\omega, \qquad (5)$$

where a is the standard deviation of the Gaussian broadening function, which describes the extent of broadening.

The second moment M_2 of the line shape can be calculated according to

$$M_2 = a^2 + \tfrac{1}{3}L^2. \qquad (6)$$

An example of the Pake doublet line shape and the corresponding FID is shown in Fig. 2. In the situation where there is more than one clearly distinguished neighbour site per nucleus, there will be an $F_P(t)$ function for each site and the resulting FID is a composite signal.

2.2. Moment expansion of the free-induction decay

An alternative approach of describing the effect of dipolar interactions is to realise that the dipolar spin
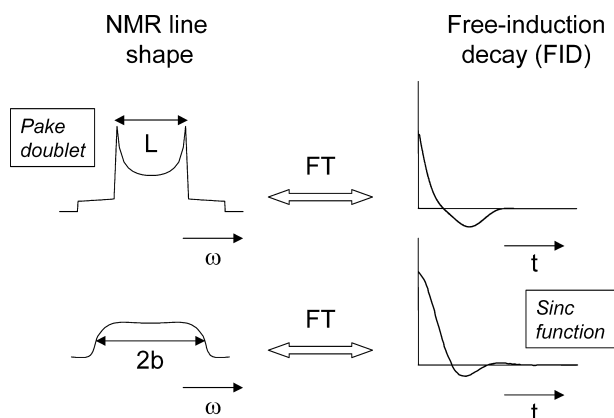
Fig. 2. Relationship between the NMR line shape and free-induction decay (FID) for a Pake doublet line shape (top) and an unresolved line shape, based on a sinc-type FID (bottom). The parameters L and b indicate the characteristic widths in the spectra and are defined by Eqs. (4) and (9), respectively. The frequency and time domains are related by a Fourier transformation (FT).

Hamiltonian is a result of a large number of dipolar interactions. This may lead to a broad NMR line shape with little or no resolved structure. Despite these difficulties, valuable structural information can be extracted through the approach of moment analysis of the line shape [15].

The nth moment M_n of a line shape function $G(\omega)$ with respect to the point ω_0 is given by

$$M_n = \frac{\int_0^\infty (\omega - \omega_0)^n G(\omega)\, d\omega}{\int_0^\infty G(\omega)\, d\omega}. \tag{7}$$

The second moment M_2 is a useful parameter in the analysis of solids [4], since it is sensitive to the "packing" of the protons in the sample. It also provides information about non-random molecular motions, since these partly average the dipolar interactions. The NMR spectrum will then still be broadened, but with a reduced second moment.

The FID can be written as a Taylor expansion in terms of the moments M_n of the line shape function:

$$F_M(t) = 1 - M_2 \frac{t^2}{2!} + M_4 \frac{t^4}{4!} - \cdots, \tag{8}$$

where the index M now refers to the moments approach.

As Abragam [11] has pointed out, this expansion bears a strong resemblance to a function, which is a combination of a sinc function $(\sin bt / bt)$ and a Gaussian broadening

$$F_M(t) = \exp\left(-\frac{1}{2}a^2 t^2\right) \frac{\sin bt}{bt}, \tag{9}$$

which has a series expansion

$$F_M(t) = 1 - \left(a^2 + \frac{1}{3}b^2\right)\frac{t^2}{2!} + \left(3a^4 + 2a^2 b^2 + \frac{1}{5}b^4\right)\frac{t^4}{4!} - \cdots \tag{10}$$

Comparison of these two expressions shows that for the second moment

$$M_2 = a^2 + \tfrac{1}{3}b^2 \tag{11}$$

and for the fourth moment

$$M_4 = 3a^4 + 2a^2 b^2 + \tfrac{1}{5}b^4. \tag{12}$$

This broadened sinc function, Eq. (9), was found to provide a good analytical description for experimental FID data [4,16]. The line shape corresponding to Eq. (9) is shown in Fig. 2. It is a rectangular line shape with a total width $2b$, convoluted with a Gaussian line shape with a standard deviation given by parameter a, which results in broadened flanks. It should be noted that both types of FIDs shown in Fig. 2 exhibit the characteristic beat pattern that is observed in many experimental cases (e.g., FID data acquired on low mobility crystalline and glassy systems).

2.3. Samples containing solid and mobile protons

Experimentally it can be difficult to assess whether the dipolar NMR spectrum exhibits a clear Pake doublet in the line shape, or a broad unresolved line shape. This arises, because generally the total line shape is a superposition of the line shapes of solid and mobile protons. In such a case, the total FID can be described by a composite function [4,5]:

$$F(t) = f_s F_s(t) + f_m F_m(t), \tag{13}$$

where the line shape of the solid protons, $F_s(t)$, is $F_P(t)$ (Eq. (5)) or $F_M(t)$ (Eq. (9)), depending on the approach taken. The parameters f_s and f_m are the fractions of solid and mobile protons, respectively.

The line shape of the mobile protons is expected to be Lorentzian, giving for the FID, the following exponential equation:

$$F_m(t) = \exp(-t/T_{2m}). \tag{14}$$

Here T_{2m} is the spin–spin relaxation time of the mobile protons.

In total line shape function $G(\omega)$, which is the Fourier transform of Eq. (13), the "trough" between the Pake doublets of the solid protons may be "filled" with a sharper line shape of the mobile protons (see Fig. 3). The challenge therefore is to find the best theoretical description for a range of experimental samples. For this, we have selected several carbohydrate samples at various moisture contents and carried out a comparative analysis, based on Eq. (13).

3. Materials and methods

For the comparison of various fitting methods, NMR data sets were used obtained by Van den Dries et al. [4] on maltose–water samples. Glucose with deuterated
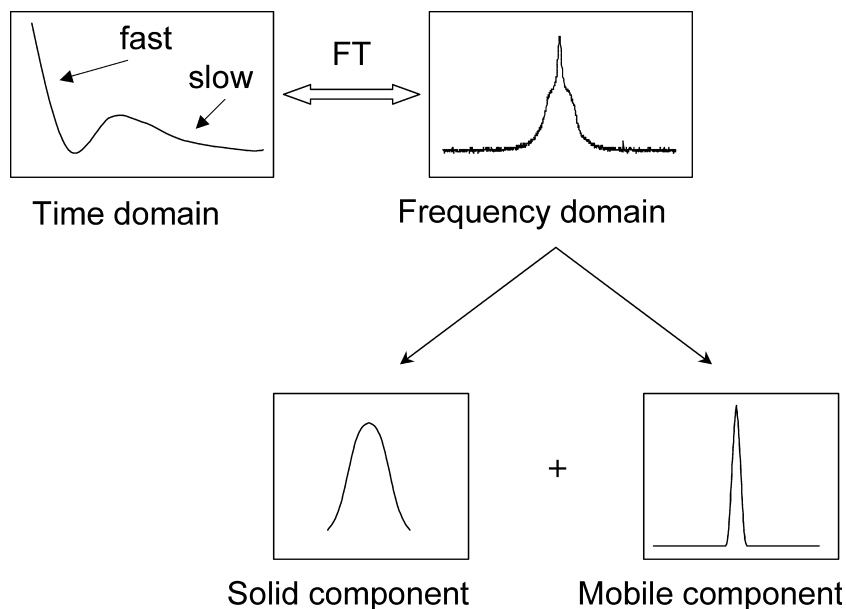
Fig. 3. Schematic illustration of a two-component NMR spectrum arising from a superposition of solid (fast component in the time domain) and mobile protons (slow component). The frequency and time domains are related by a Fourier transformation (FT).

hydroxyl groups was prepared by dissolving the mono-hydrate (1 g) in D_2O (5 ml) and subsequently freeze-drying before adjusting the water content with D_2O. The D_2O content was adjusted to 10 wt%.

^{1}H NMR measurements were performed on a Bruker AMX 300 spectrometer equipped with a Bruker 5-mm proton probe operating at a resonance frequency of 300.13 MHz. The temperature was regulated with a ni-trogen temperature control. The temperature stability was within 0.5 K. A spectral width of 500 kHz was used. The duration of the 90° pulse was 6–7 μs. The FIDs are the averages of 8 scans having 2048 data points.

Fitting of the experimental NMR data was carried out using a purpose-written computer program developed using IDL and compiled Quick Basic routines imple-menting Eqs. (5), (9), and (13). Comparison of different fitting models is based on the accuracy of the fit by using the least-square deviation χ^2, which is defined by

$$\chi^2 = \frac{1}{N} \sum_i (S_i - F_i)^2, \tag{15}$$

where S_i and F_i are the experimental and calculated (Eq. (13)) data points, respectively, and N is the number of points. This method can only be used within the same data set because this definition of χ^2 is not corrected for the effect of signal/noise ratio. It should be noted that χ^2 is an all-embracing statistical description. It does not provide information about the accuracy of the fitting parameters.

4. Results and discussion

In the present work, we have confined ourselves to an analysis of the quality of fits for different models, not to the behaviour of the parameters extracted. For maltose–water systems the extracted parameters, such as the second moment M_2 and the ratio of solid and mobile protons (f_s/f_m), have been discussed in previous work [4]. In all situations examined, we visually inspected both the FIDs and NMR spectra for the presence of beats (FID) and dipolar splittings (NMR spectrum), and based the starting values of the fits on the features found. Especially the initial guess of the parameter L in the Pake fit (Eq. (5) in combination with Eq. (13)), and of the frequency b of the sinc fit (Eq. (9) in combination with Eq. (13)) were found to be of critical importance in leading to satisfactory fitting convergence.

Concerning the robustness of the fit parameters, it could be well believed that a peak sitting in the trough of a Pake doublet or on a flattened top would make the fitting difficult. Presumably a range of parameters might do an equally good job when compared with fitting simple Gaussian and Lorentzian functions. In this sense, a least-squares goodness of fit probably does not pro-vide a complete description. However, answering this question satisfactorily would involve statistical argu-ments of a very high order, which is outside the scope of this article. Therefore, our approach strongly relies on the visual inspection of the line shapes and FIDs, as outlined above.

The fitting result of a typical FID of a freeze-con-centrated 20% maltose–water system is shown in Fig. 4. It can be seen that the sinc fit properly describes the beat, while the Pake fit is not able to give a good fit. A further comparison of the Pake fit and the sinc fit for this system is shown in Fig. 5. Over a temperature range from 210 to 240 K, the sinc fit provided better results for
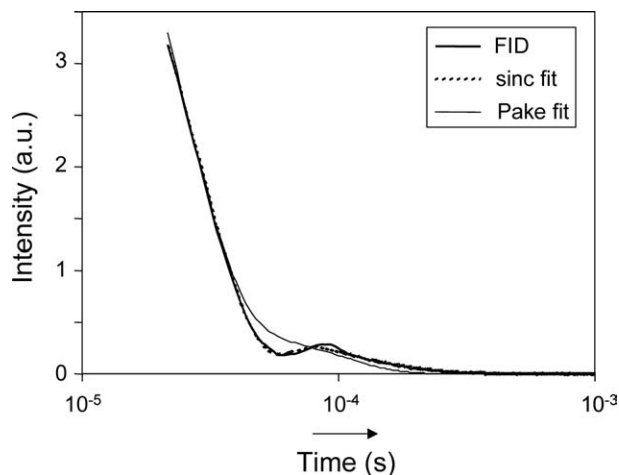
Fig. 4. Typical FID of a freeze-concentrated maltose–water glass at 215 K and the optimised sinc fit and Pake fit of the FID.
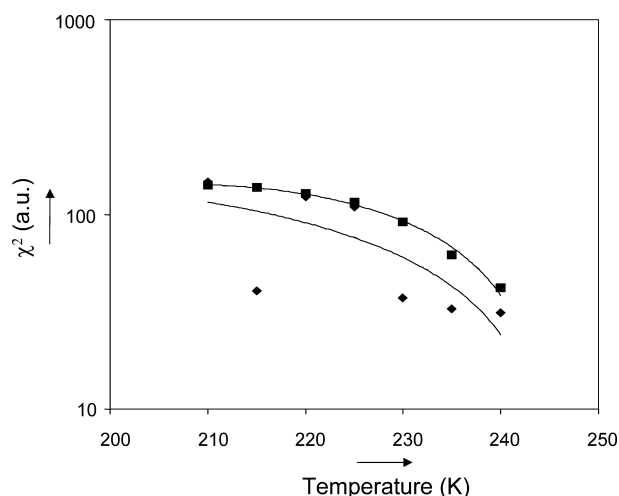

Fig. 5. Typical plot of χ^2 against temperature of the maltose–water system shown in Fig. 4. (■) Pake fit; (◆) sinc fit. The solid lines give the second order trend lines generated using MS Excel.

Fig. 6. FID (A) and corresponding NMR spectrum (B) of a freeze-concentrated 10% glucose–D_2O sample at 260 K.

this sample. This is also found in most other freeze-concentrated maltose–water systems studied. Therefore in such systems, the sinc fit is most suitable method to extract the experimental parameters.

A different situation arises when the 10% glucose–D_2O sample is considered. This is illustrated in Fig. 6, where the FID and NMR spectrum of this sample are shown. The NMR spectrum clearly shows a dipolar splitting, suggesting that the Pake fit would be most suitable. This is expected, because as compared to the maltose–water samples, in the glucose–D_2O samples the hydroxyl groups are deuterated, which will result in a more limited spread of proton–proton near neighbour distances. This also suggests that a single Pake fit would be best, despite the fact that there will still be some variation due to the off ring protons, the possibility of transition between axial and equatorial conformations
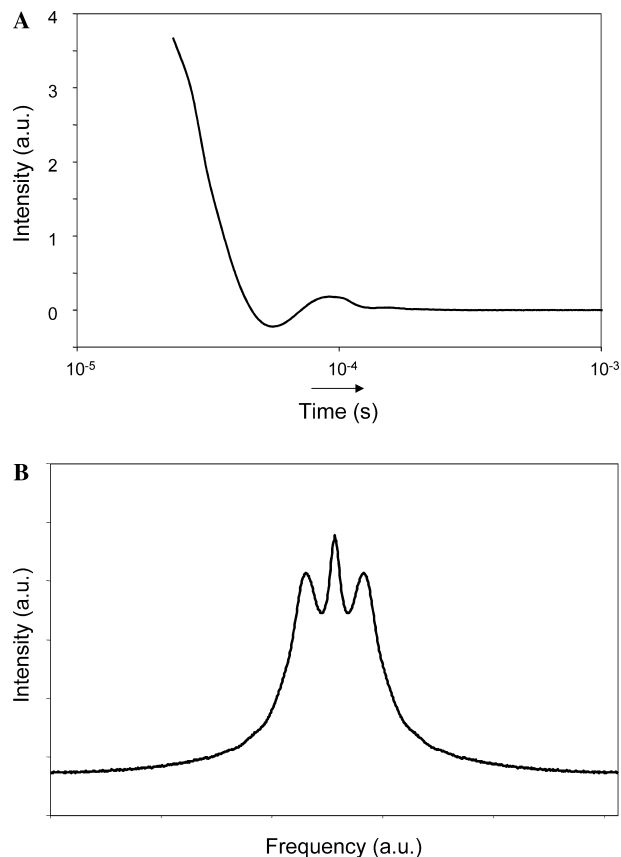
and contribution of the remaining water. As is seen in Fig. 7, the sinc fit is not satisfactory in this case, as expected, but the single Pake fit is inferior to the double
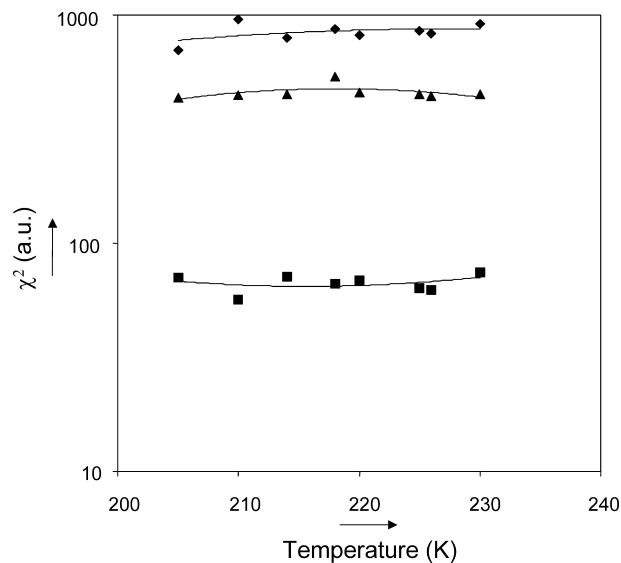

Fig. 7. Typical plot of χ^2 against temperature for the glucose–D_2O sample from Fig. 6. (◆) sinc fit, (▲) single Pake fit, and (■) double Pake fit. The solid lines give the second-order trend lines generated using MS Excel.
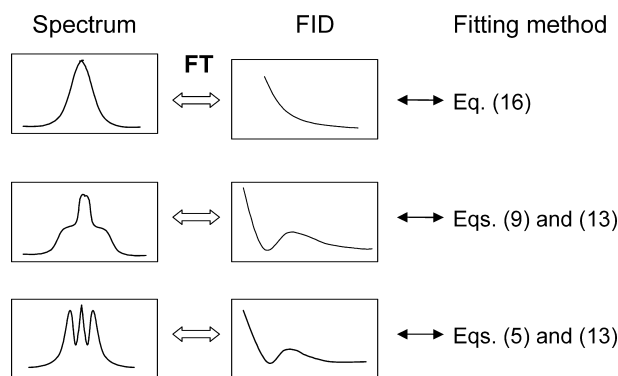
Fig. 8. Summary of fitting methods for the NMR analysis of concentrated carbohydrate–water samples.

Pake fit. The double Pake fit corresponds to L values of 0.85 and 1.20, which transform to distances of 1.6 and 1.8 Å, respectively (see Eq. (4)). This is a surprising result, which probably is related to the fact that the NMR spectrum actually is not a superposition of Pake patterns of proton pairs. In fact it arises from the mutual dipolar interaction of several protons, as given by Eq. (1).

5. Conclusions

NMR analysis of glassy freeze-concentrated carbohydrate–water samples is still a complex field of research. A general approach for the analysis of FIDs and NMR spectra cannot be given. Nevertheless, based on the present work a couple of useful rules of thumb emerge. The application of these rules requires a critical inspection of both the FIDs and NMR spectra as is summarised in Fig. 8.

In most cases the sinc fit gives satisfactory results and provides useful information about the second moment M_2 and the ratio of solid and mobile protons (f_s/f_m). A good indication for using the sinc fit is the presence of a beat in the FID and absence of a Pake pattern in the NMR spectrum. At increasing temperatures this approach breaks down due to the increase of motion in the system. In this case a biexponential fit as given by

$$F(t) = f_s \exp(-t/T_{2s}) + f_m \exp(-t/T_{2m}) \qquad (16)$$

will then be more appropriate [4].

If a clear dipolar splitting is observable in the spectra, the Pake fit (or a multiple Pake fit) should be used. Also

in this case information about M_2 and f_s/f_m can be obtained.

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