Determination of MG and TG Phase Composition by Time-Domain NMR

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ABSTRACT: The feasibility of time-domain NMR curve-fitting methodology for the quantitative determination of TG blend phase compositions was investigated. By studying a range of TG in their different crystal forms, it was shown that the transverse NMR relaxation characteristics of TG differ for the respective crystal polymorphs {α,β,β'}. This enables the TG polymorphism in fat blends to be quantitatively determined by curve fitting. If a liquid phase is present in the blend, curve fitting is able to determine the solid fat content, and the results compare well with those of the accepted NMR methods. The curve-fit method is less hindered by some of the disadvantages of these accepted methods, such as the use of a calibration factor.

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KEY WORDS: Crystal polymorphs, monoglycerides, phase behavior, relaxometry, solid fat content, time-domain NMR, triglycerides.

In food technology, the phase composition of fats and oils is an important parameter in process control (1), fat blending properties, and assessments of the quality of various products (2,3). Dilatometry, which is based on the difference in density between the solid and liquid phases, has for a long time been the dominant method to measure the solid fat index (SFI) (4), but this method is laborious and time consuming. Time-domain nuclear magnetic resonance (TD-NMR) has now become the dominant technique, as it offers many advantages regarding speed and ease of operation (2,5,6) and accurate information on the solid–liquid ratio (7,8).

The current TD-NMR methods for SFC determination of fat blends have been successfully applied in fat technology for several decades. On one hand, the indirect method (2,7) is considered accurate but not precise, whereas, on the other hand, the "direct" method (2,5) is precise but not accurate and needs a calibration factor (derived from plastic-in-oil samples). In the hands of a skilled operator, the solid-echo (8) method is considered to be both accurate and precise but has never caught on in routine laboratories. Despite its obvious limitation, the direct method has become the most widespread method for SFC determination due to its ease of use and its high precision. However, since the introduction of this direct SFC method in the 1970s, the specifications of commercial TD-NMR equipment have improved dramatically. Also, there is a belief that the current methods do not fully exploit the potential of modern technology.

In the detergent area, several applications have been described that show how the phase behavior of surfactants can be assessed by curve fitting of the time-domain data (9). So far, only a few examples are known where the phase behavior of lipids has been assessed (10,11). In recent reports (12,13), it was demonstrated that curve fitting of rapidly sampled transverse NMR relaxation decay curves enabled the quantitative determination of the mesomorphic state of polysaccharides. As the curve-fitting method is not fraught with some of the disadvantages of the current SFC NMR methods, we have embarked on a study to investigate the feasibility of curve fitting for quantification of MG and TG phase compositions. First, we will show that, using curve fitting, we can obtain TG SFC values without using an external calibration factor. Second, we will demonstrate that information regarding TG polymorph composition can be obtained in a quantitative manner.

Free induction decay NMR line shapes. For MG and TG, we can distinguish three basic polymorphic forms, α, β, and β', which differ in carbon-chain packing and dynamics (14, 15,16). The transverse relaxation behavior of their NMR signals is sensitive to these differences in molecular dynamics (17). In this study, we will distinguish three different mobility regimes, which can be described by Lorentzian, Gaussian, and Pake functions. Lorentzian (exponential) functions (17) are used to characterize the TD-NMR signal of a liquid phase where spins experience a high degree of mobility. The time constant T_2 in a Lorentzian function, $L(t)$, is for a liquid typically in the millisecond to second range. We note that in inhomogeneous magnetic fields, such as those encountered in most commercial low-field TD-NMR spectrometers, one can rarely observe liquid Lorentzian (exponential) decay functions. Commonly, one observes a signal in which the Lorentzian signal is multiplied by Gaussian field inhomogeneity functions (10,11). The field inhomogeneity can be removed, however, by application of a Carr–Purcell–Meiboom–Gill pulse train, thus producing pure Lorentzian decays again (9). Gaussian functions are characteristic for solid phases that still have molecular mobility, such as semisolid ("amorphous") phases, liquid crystals, or crystal phases with high degrees of mobility (e.g., α-polymorphs).

The time constant T_2 in a Gaussian function, $G(t)$, typically ranges from 10 (solids) to 100 µs (liquid crystalline states or semisolid amorphous phases). Pake functions are the theoret-

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ical models used to characterize solid phases in a rigid crystalline form (17,18), such as the β′- and β-polymorphs. The decay function depends on the orientation of the crystal cell relative to the magnetic field. In Equation 1, the integration serves to account for all crystal orientations:

$$P(t) = P_0 x_0 \int_0^{\pi} d\theta \times W \times \cos\left[\omega_D \times \mathrm{Op}\right] \times \exp\left[-t^2/2 \times \left(m_2 \mathrm{Op}^2 + B^2\right)\right] \quad [1]$$

where θ is the orientation angle of the microcrystal; m_2 is the second moment, which is correlated with the mobility of protons in the crystal lattice; Op is the order parameter, typically $P_2(\cos\theta)$; W is the weighing factor, typically sinθ; ω_D is the dipolar coupling constant, i.e., strength of the dipolar interaction between protons in the crystal; and B is the orientation-independent Gaussian line-width parameter. The line shape described by Equation 1 takes into account all relevant relaxation parameters and is able to give a complete description of the decay curve of solid materials. We also note that more empirical descriptions of such line shapes have been used (12,19), but these do not use parameters of physical relevance (i.e., m_2 and ω_D).

In fat blends, all different mobility regimes can exist at the same time, and the NMR signal decay is an ensemble of Lorentzian, Gaussian, and Pake functions (Eq. 2). By fitting $S(t)$ to experimental free induction decays (FID), the phase composition (p_i, g_j, and l_k) can be obtained:

$$S(t) = \sum_i p_i P_i(t) + \sum_j g_j G_j(t) + \sum_k l_k L_k(t) \quad [2]$$

We will show that for the different forms, the relaxation parameters fall into distinctive regions. This allows these parameters to be constrained, hence making the fitting process more reliable.

EXPERIMENTAL PROCEDURES

Fat blends. TG were either homemade (>98% purity) or purchased commercially (Sigma-Aldrich, St. Louis, MO; >98% purity), and samples were used without any further purification. TG are abbreviated as PPP (1,2,3-palmitin), SSS (1,2,3-stearin), MPS (1-myristin-2-palmitin-3-stearin), LLL (1,2,3-laurin), MMM (1,2,3-myristin), PPP (1,2,3-palmitin), LPP (1-laurin-2,3-palmitin), PSM (1-palmitin-2-stearin-3-myristin), POP (1,3-palmitin-2-olein), MSS (1,2-stearin-3-myristin), PSP (1,3-palmitin-2-stearin), and MPM (1,3-myristin-2-palmitin). MG (1-palmitin) was obtained from Quest International (Zwijndrecht, The Netherlands) and was of >95% purity. The α-modifications of MG and TG were made by a rapid cooling of a melt on a cold metal surface. The crystal forms were checked by X-ray diffraction (XRD). Commercial fat blends extracted from consumer and bakery margarines were prepared from commercial spread products by separation of the fat phase from the water phase. The original product was melted and filtered using Na_2SO_4 to eliminate the water phase, and only the fat phase was analyzed. Also, hardstock blends with a high SFC value (>50%) were used. Samples were tempered before each measurement.

Tempering procedures. NMR tubes were filled to either 1- (indirect method) or 3-cm (other methods) height, and the samples were tempered before each measurement. The extended tempering scheme from the AOCS official method (20) was used, i.e., melting at 80°C, 5 min (at 60°C), 16 h (at 0°C), 30–35 min (at 10°C), and subsequent measurement at 10°C.

NMR data acquisition and processing. The time-domain data were obtained on a Bruker NMS120 Minispec spectrometer (Rheinstetten, Germany) using a custom-written pulse program (Bruker Exspel programming language). The samples were measured at controlled temperature using a thermostated probe head. Calibration of the F-factor was done using plastic-in-oil standards, and important parameters were checked every 24 h: temperature and homogeneity of the magnet, magnetic field tunings, detection angles, and pulse lengths. The signal decays were recorded at 0.1 μs intervals between 9 and 100 μs. The experimental data were analyzed by fitting to theoretical functions (see the Introduction section) using TableCurve® 2D software (21). Errors of the fitted parameters are given as the inverse values of the diagonal elements of the covariance matrix, or are defined as so-called elliptical errors that take into account the off-diagonal elements (i.e., covariance between parameters) (22). The indirect and direct SFC reference measurements were carried out according to AOCS official methods (2,20).

X-ray diffraction data acquisition. X-ray diffractograms for the present work were measured using a Delft Instruments (Delft, The Netherlands) CPS120 diffractometer equipped with a position-sensitive counter, an FR590 generator with an X-ray tube, and an Anton Paar (Graz, Austria) temperature control unit. The X-ray tube with copper anode was operated at 50 kV and 40 mA. The wavelength of the Cu Kα radiation was 1.5418 Å.

RESULTS and DISCUSSION

Line shape analysis for typical (model) TG. Except for an early attempt using scanning NMR techniques (23), no detailed and systematic NMR line-shape analysis has been performed on TG polymorphism. To obtain insight into the range of the NMR relaxation parameters, several TG with known crystal polymorphic behavior were measured. We selected TG that were known to be stable in β- and β′-forms (24). α-Modifications were also prepared from these TG using a simple tempering treatment (see the Experimental Procedures section). We have recorded NMR decay curves of these crystal forms, and typical examples are shown in Figure 1. Here, the α- and β-forms were made from SSS and the β′-form from PSP. It is clear that the line shape is different for each modification. Subsequently, we have fitted the decay curves with theoretical functions (see the Introduction section). It was found that decays of α-polymorphism could be fitted with a Gaussian function and β and β′ polymorphs could be approximated with Pake functions. To obtain a better description of the experimental line shapes, the Pake function, $P(t)$, in Equation 1 was empirically adjusted by taking Op = cosθ and $W = 1$. Thus, the ω_D and m_2 parameters obtained from fitting

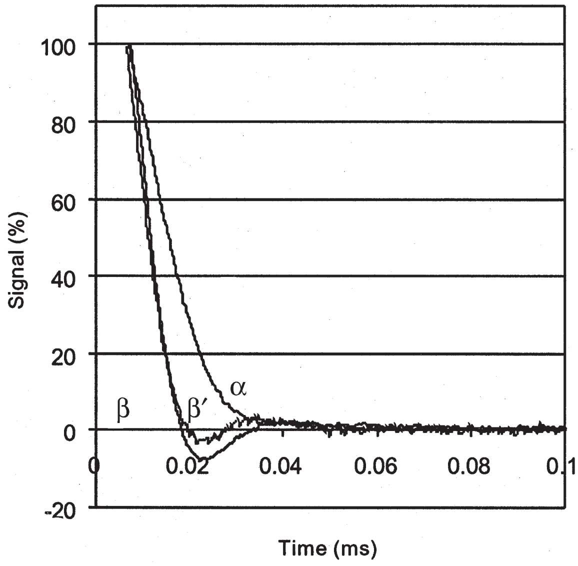

FIG. 1. Decay curves of different TG crystal forms (α and β, SSS; β′, PSP).

Equation 1 to the experimental data are semi-empirical. Hence, these values should be considered as a measure for the true dipolar coupling and second moment. From these values, the averages of each parameter were calculated. These are shown in Table 1, with their deviations, expressed in percentages.

From Table 1, we can observe that the β- and β′-forms had ω_D and B values that fell into the same range. The principal difference observed between β- and β′-modifications was the m_2 value, which was higher for the β′- than for the β-form. This meant that the respective crystal forms for a wide variety of TG were similar; hence, we could use the average relaxation parameters (Table 1) to describe the typical line shapes of β-, β′-, and α-polymorphs. This was observed previously in an NMR study that employed scanning techniques (23). In that study, the second moments found for a range of TG followed the same trend as found here.

The observations made here imply that by fixing the relaxation parameters in the Gaussian and the Pake functions, we could define specific line shapes for each polymorphic form, decrease the degree of freedom during the fitting, and obtain quantitative phase compositional data.

TABLE 1
Average NMR Relaxation Parameters for TG Polymorphs[a]

Crystal form	ω_D (kHz)	m_2 (kHz^2)	B (μs)	T_2 (μs)
β	147 ± 6	$(4.5 \pm 0.2)\ 10^3$	25 ± 2	
β′	146 ± 4	$(5.4 \pm 0.2)\ 10^3$	24 ± 1	
α				11.8 ± 0.2

[a] The average values were obtained from a series of TG compounds crystallized in the α-form (PPP, SSS, MPS, LPP), the β-form (LLL, MMM, PPP, SSS, LPP, PSM, MPS, POP), and the β′-form (MSS, PSP, MPM). PPP, 1,2,3-palmitin; SSS, 1,2,3-stearin; MPS, 1-myristin-2-palmitin-3-stearin; LLL, 1,2,3-laurin; MMM, 1,2,3-myristin; PPP, 1,2,3-palmitin; LPP, 1-laurin-2,3-palmitin; PSM, 1-palmitin-2-stearin-3-myristin; POP, 1,3-palmitin-2-olein; MSS, 1,2-stearin-3-myristin; PSP, 1,3-palmitin-2-stearin; and MPM, 1,3-myristin-2-palmitin. TG were either homemade or purchased from Sigma-Aldrich (St. Louis, MO). ω_D, dipolar coupling constant; m_2, second moment; B, orientation-independent Gaussian line width parameter; T_2, transversal relaxation time (see text).

{α,β} polymorph composition of a model TG system. To investigate the feasibility of determining crystal polymorphs in a quantitative manner, we prepared samples with a known {α,β} composition. The α-modification of tristearin (SSS) was prepared (see the Experimental Procedures section) and immediately mixed with the stable form (β-modification). The FID were recorded by TD-NMR, and the decay curves are presented in Figure 2. The curves were fitted and were found to consist of mixtures of a single Gaussian (G_1) and a single Pake (P_1) function. Different parameters for each function were fixed by fitting a pure α-form for the Gaussian function (T_2) and a pure β-form for the Pake function (ω_D, m_2, and B). The existence of the pure modifications was verified at the same time by XRD. NMR signal decay curves were fitted by such a mixed function (Gaussian and Pake functions, G_1 and P_1, respectively), and the amplitudes of each function were determined. No liquid phase was taken into account because SSS is a pure solid at room temperature. The percentage of each form ([α)], [β], [β′]) was determined using an equation of the form:

$$[\alpha] = \frac{g_1 G_1}{g_1 G_1 + p_1 P_1} \times 100 \qquad [3]$$

In Figure 3, the percentages of α-modification, [α], determined by curve fitting are represented as a function of weighed-in values during preparation. These are considered to be the real values. The straight line corresponds to the real percentages of the α-form, and the values determined using the curve-fitting method are represented by the points. We can see that results from curve fitting are in good correspondence with the weighed-in (real) values. Thus, we can conclude that the curve-fitting method can distinguish α- from β-polymorphs in a quantitative manner and that it is possible to calculate accurately and precisely their relative percentages.

{β,β′} polymorph composition of a model TG system. To investigate the ability of TD-NMR for quantitative discrimi-

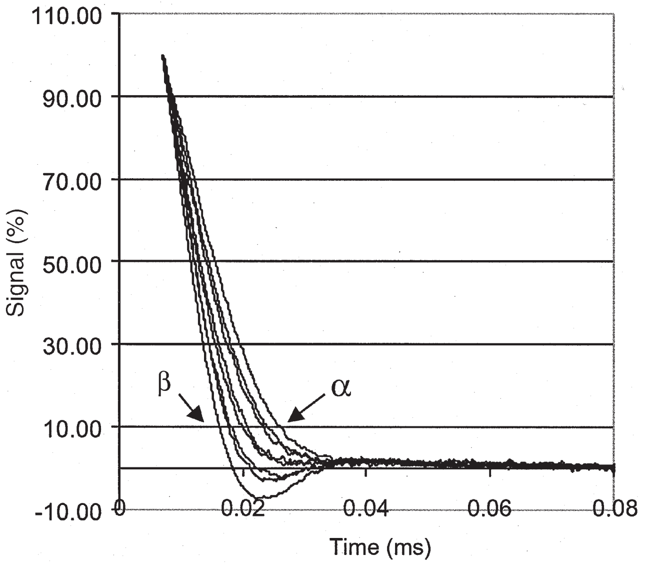

FIG. 2. NMR signal decays of α,β blends. The pure α and β form have been indicated in the text.

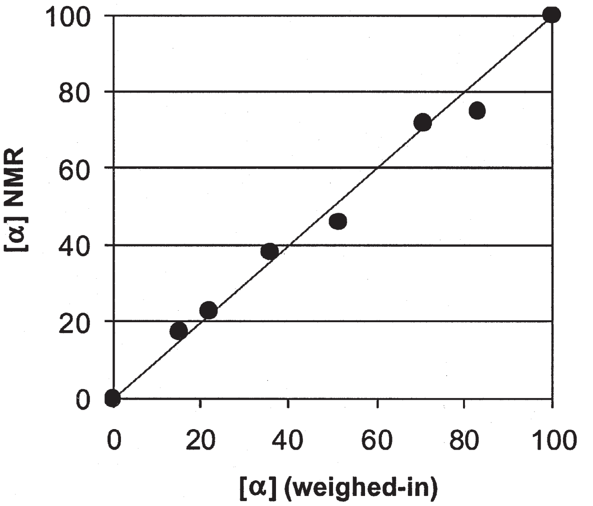

FIG. 3. Relative amount of α-form, [α], in an {α,β} system as determined by curve fitting. The reference axis represents weighed-in values.

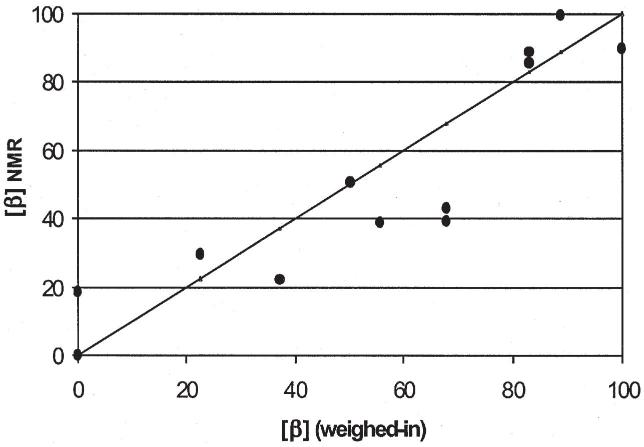

FIG. 4. Relative amount of [β] in a {β,β′} system as determined by curve fitting (the reference axis pertains to weighed-in values). Values are given as a function of the weighed-in amount (w/w%) of SSS in SSS (β)–PSP (β′) mixtures.

nation of β- from β′-modifications, transverse signal decays of mixtures of two different TG were recorded. SSS and 2-stearodipalmitin (PSP), which are known to be the most stable in β- and β′-forms, respectively, were first tempered according to the extensive regime described in the Experimental Procedures section. The crystals were then mixed (without additional temperature treatment) in different ratios, by weight (and corrected for the different proton contents of the two species). The decay curves were analyzed by curve fitting using a single Pake function. The results for pure SSS and pure PSP were used to fix the parameters, ω_D and B, in the fitting of the different mixtures of β and β′-forms. For the different mixtures of SSS and PSP, the (mean) second moment, m_2, of the Pake function was the parameter determined during the fitting; we can calculate an approximate value of {β,β′} composition using Equation 4:

$$[\beta] = \frac{m_2[\beta,\beta'] - m_2(\beta')}{m_2(\beta) - m_2(\beta')} \times 100 \qquad [4]$$

Here, $m_2[\beta,\beta']$ is the mean second moment of the mixture, from which we determined the relative content of the β-form, [β′]. The results are shown in Figure 4 as a function of the weighed-in values of the β-form (corrected for the number of protons in PSP and SSS). We can see that an increase in the amount of β-form is accompanied by a decrease in $m_2[\beta,\beta']$. It is clear that $m_2[\beta,\beta']$ depends on the amounts of β- and β′-forms present in the samples. We concluded that we could distinguish the β- from the β′-form in a quantitative manner. However, a comparison of Figures 3 and 4 shows that the determination of [β] in a {β,β′} system is less precise than for the α-form in an {α,β} system. As can be seen in Figure 1, this can be attributed to the smaller difference in line shapes between the β- and β′-forms, compared to the α- and β-forms.

Crystal polymorph transition kinetics in a MG system. Bulk MG with a small amount of DG impurity show a relatively simple phase behavior when a melt is rapidly cooled. At first, a MG α-crystal polymorph is formed in which most of the DG species are dissolved. Subsequently, the MG converts to the β-crystal form and the DG is expelled from the crystal lattice, thus forming a liquid-like phase. In this study, the slow conversion of the α- to the β-polymorph and the formation of a liquid phase was monitored by TD-NMR. The FID were fitted with the sum of a Pake function (P_1) and two Gaussian functions, one with a time constant constrained to a value in the solid regime (G_1, <100 s) and one in the liquid range (G_2, >100 s). The functions P_1 and G_1 describe the β- and α-polymorphs, and G_2 describes the liquid component present. The result is presented in Figure 5, where one can observe a transition of the α-polymorph to the β-form, and also the formation of a small amount of liquid phase. To assess the accuracy of these values, the α-to-β MG transition was also monitored by means of DSC and XRD (also shown in Fig. 5); this demonstrated that the TD-NMR results were in good agreement with DSC data. The XRD experiment resulted in different values, which were caused by peak separation prob-

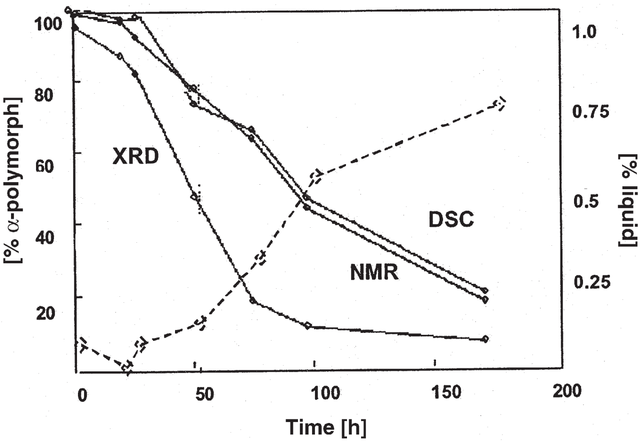

FIG. 5. α- to β-Crystal transition kinetics of MG as monitored by TD-NMR, DSC, and XRD. Solid lines are referenced at the left axis, with the dashed line, which corresponds to the amount of liquid component, referenced at the right axis.

lems between α and β in the diffractogram and the presence of small crystals that may not have been observed by XRD. Hence, compared to DSC, TD-NMR had the advantage that it was nonperturbing, and, relative to XRD, it was a cheaper technique and easier to handle.

Commercial fat blend phase compositions. To compare curve fitting with the conventional direct SFC method, a measurement scheme was set up with a range of fat blends. We chose 25 commercial margarine fat blends, representing a good contemporary survey of the global margarine market. In addition, 7 bakery margarines and 10 hardstock blends were selected on the basis of their hard fat content (high melting temperatures). All blends were subjected to an extended tempering scheme (see the Experimental Procedures section) and were measured at 10°C. In Figure 6, the results of the curve-fitting and direct methods are presented in the form of a scatterplot. The results from the indirect method were considered most accurate (2); the corresponding values were plotted on the horizontal (reference) axis. Differences between the reference and other methods (curve fitting and direct) were calculated for each sample and are expressed in percentages. In Figure 6, we can observe small systematic deviations between direct and indirect (reference) SFC values. Especially for hardstocks and bakery margarine blends, the direct SFC values tended to be too low. This effect was most pronounced at the low temperature (10°C) and/or when the long tempering scheme was used. Under these conditions, these materials had enhanced transverse relaxation properties, which were not adequately described by the use of an "average" calibration *F*-factor (2,5). The SFC values obtained from curve fitting were less affected by the polymorphic variation. Thus, we can conclude that this method gave more accurate results.

Also, attempts have been made to assess the polymorphic state of the blends directly, as was done for the two-component blends (*vide supra*). However, the large number of functions (and DF) needed to fit the NMR decays increased the error on the polymorphic composition and no meaningful results could be obtained.

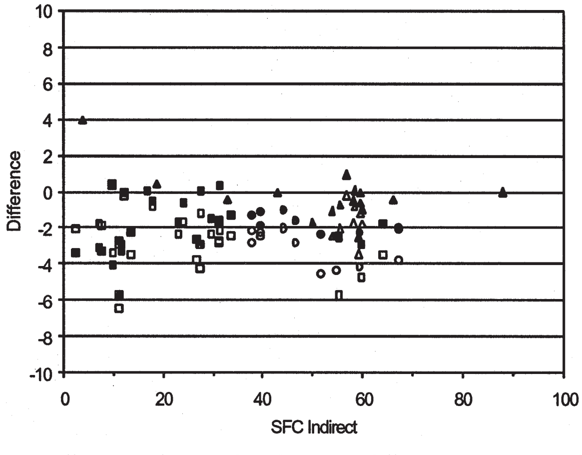

FIG. 6. Difference of SFC values between different TD-NMR methods (open symbols: direct; closed symbols: curve fitting; reference: indirect method). Margarine blends (□), hardstocks (○), and bakery margarine blends (△) were incorporated in the measurement scheme.

An issue that was not addressed in this study was the presence of amorphous phases. It is well known that such phases, with a significant degree of molecular mobility ($T_2 \approx 50–100$ μs), can exist, depending on blend composition and thermal history (10,11). Indeed, such species with long relaxation times have been observed and are in the order of approximately 1% for the vegetable fat blends used here (depending on thermal history). Taking this phase into account in the curve fitting will enhance the accuracy of the method and lead to a more complete description of the fat blend system.

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