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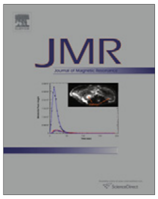

Signal intensities in ^{1}H–^{13}C CP and INEPT MAS NMR of liquid crystals

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ABSTRACT

Spectral editing with CP and INEPT in ^{13}C MAS NMR enables identification of rigid and mobile molecular segments in concentrated assemblies of surfactants, lipids, and/or proteins. In order to get stricter definitions of the terms "rigid" and "mobile", as well as resolving some ambiguities in the interpretation of CP and INEPT data, we have developed a theoretical model for calculating the CP and INEPT intensities as a function of rotational correlation time τ_c and C–H bond order parameter S_{CH}, taking the effects of MAS into account. According to the model, the range of τ_c can at typical experimental settings (5 kHz MAS, 1 ms ramped CP at 80–100 kHz B_1 fields) be divided into four regimes: fast ($\tau_c < 1$ ns), fast-intermediate ($\tau_c \approx 0.1$ μs), intermediate ($\tau_c \approx 1$ μs), and slow ($\tau_c > 0.1$ ms). In the fast regime, the CP and INEPT intensities are independent of τ_c, but strongly dependent on $|S_{CH}|$, with a cross-over from dominating INEPT to dominating CP at $|S_{CH}| > 0.1$. In the intermediate regime, neither CP nor INEPT yield signal on account of fast $T_{1\rho}$ and T_2 relaxation. In both the fast-intermediate and slow regimes, there is exclusively CP signal. The theoretical predictions are tested by experiments on the glass-forming surfactant *n*-octyl-*β*-D-maltoside, for which τ_c can be varied continuously in the nano- to millisecond range by changing the temperature and the hydration level. The atomistic details of the surfactant dynamics are investigated with MD simulations. Based on the theoretical model, we propose a procedure for calculating CP and INEPT intensities directly from MD simulation trajectories. While MD shows that there is a continuous gradient of τ_c from the surfactant polar headgroup towards the methyl group at the end of the hydrocarbon chain, analysis of the experimental CP and INEPT data indicates that this gradient gets steeper with decreasing temperature and hydration level, eventually spanning four orders of magnitude at completely dry conditions.

1. Introduction

Comparing ^{13}C MAS NMR spectra acquired with CP [1] and INEPT [2] ^{1}H–^{13}C polarization transfer is a convenient way of obtaining site-resolved qualitative information about molecular segment dynamics [3–6]. We have recently demonstrated the utility of the CP/INEPT approach for studying surfactant [7] and lipid [8] phase behavior in the low water content regime, in which the temperature-composition phase diagram is dominated by two-phase areas with coexistence between various solid- and liquid crystalline phases. In the context of surfactant science, we have used the name polarization transfer solid-state NMR (PT ssNMR) for our way of displaying ^{13}C MAS spectra acquired with CP, INEPT, and ^{13}C direct polarization (DP). By color-coding and overlaying the three spectra, one can at a glance assign the resolved ^{13}C resonance lines to molecular segments residing in solid, isotropic liquid, or anisotropic liquid crystalline phases. The robustness, short acquisition time, and ease of interpretation of the PT ssNMR experiment makes it a useful tool also for non-expert NMR users studying surfactant or lipid phase behavior over wide ranges of conditions, e.g., chemical composition, temperature, and humidity, using samples at natural isotopic abundance.

We have developed a simplified theoretical model for predicting the signal intensities obtained with CP and INEPT under MAS for anisotropic liquid crystalline systems, where the dynamics and the anisotropy of C–H bond reorientation are quantified with the rotational correlation time τ_c and the order parameter S_{CH}, respectively [7]. According to the model, INEPT gives signal enhancement for isotropic liquids with $\tau_c < 10$ ns and $|S_{CH}| < 0.05$, while CP is most efficient for solids with $\tau_c > 10$ μs and/or $|S_{CH}| > 0.5$. For anisotropic liquid crystals, where $\tau_c < 10$ ns and $0 < |S_{CH}| < 0.3$, there is a continuous transition between dominating INEPT to dominating CP when increasing $|S_{CH}|$. In the intermediate time regime, around $\tau_c = 1$ μs, neither CP nor INEPT yield signal because of unfavorable relaxation rates. In recent and ongoing projects dealing with phase behavior and nanostructure of lipids and proteins in the *Stratum corneum* [9], the outermost layer of the skin, we have noticed the need for a more detailed investigation of the intermediate regime, addressing issues such as the range of τ_c for which both CP and INEPT are inefficient and the order of appearance of CP and INEPT signals when entering the regime with

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fast dynamics. Hence, we here present a refined version of the theoretical model. We compare the predictions of this model with measurements on an anisotropic system where τ_c can be varied continuously in the relevant range.

The system chosen for the experimental studies is *n*-octyl-β-D-maltoside (C_8G_2), a surfactant consisting of a maltose hydrophilic headgroup and an octyl hydrophobic tail as shown in Fig. 1. C_8G_2 belongs to the class of alkyl (poly)glycoside surfactants (C_xG_y), which find wide applications in cosmetics, manual dishwashing, and detergency because of their surface activity [10], biodegradability, and low toxicity [11]. Calorimetry and small-angle X-ray scattering have shown that C_8G_2 and $C_{14}G_2$ exhibit glass transitions at low water content [12,13], which is a rather unusual feature for simple surfactant systems, although possibly more common for phospholipids as recently proposed by Shalaev et al. [14]. Glasses or amorphous phases are traditionally observed for polymers, where the complicated molecular structure prevents an ordered molecular packing and the formation of a crystalline solid [15]. Extensive research has been conducted on polymer glass transitions [16,17] as it affects the material properties, such as flexibility and toughness. In the C_8G_2 case, the bulky headgroup is thought to be the reason for the formation of an amorphous instead of a solid crystalline phase [12]. The glassy state of C_8G_2 can be considered as a frozen form of the corresponding lamellar liquid crystalline phase, and is thus more appropriately called “glassy crystalline state” as suggested by Kocherbitov and Söderman [12]. Whereas transitions between liquid and crystalline phases occur at a well-defined temperature and are accompanied by a jump of τ_c and S_{CH}, glass transitions involve a continuous change of τ_c by several orders of magnitude over a narrow temperature interval while the structure remains essentially unchanged [15]. Small-angle X-ray scattering measurements on C_8G_2 have shown that there is only a negligible change in the lamellar repeat distance when cooling the liquid crystalline phase into the glassy crystalline state [12]. This observation supports the view that the C_8G_2 glass transition occurs without structural changes. By varying the temperature and hydration level of C_8G_2, a wide and continuous range of τ_c is conveniently accessible for experimental studies.

A trend of decreasing τ_c and $|S_{CH}|$ from the polar headgroup towards the end of the hydrocarbon tail arises on account of the anchoring of the headgroup at the hydrophilic–hydrophobic interface [18]. Thus, when changing the dynamics of the whole system by varying the temperature or the water content, it is possible to find conditions where the different parts of the C_8G_2 molecule are in different dynamical regimes with respect to polarization transfer efficiency. In addition, a single correlation time is not sufficient to describe the decay of the rotational correlation function since segment reorientation occurs on a wide range of time scales due to mechanisms such as hydrocarbon chain isomerization, as well as molecular rotation, wobble, and translational diffusion. In order to aid the analysis of the experimental PT ssNMR data, we perform near-atomistic molecular dynamics (MD) simulations of the C_8G_2/H_2O system in the fast/intermediate dynamics regime. The MD simulations yield detailed information about C–H bond reorientation anisotropy and dynamics, which we quantify as a continuous distribution of correlation times $P(\tau_c)$ for each carbon site. Based on the well established procedures for calculating ^{13}C T_1 and ^1H–^1H cross relaxation rates directly from the MD trajectories [19,20], we propose a method for estimating PT ssNMR signal intensities from the simulated $P(\tau_c)$.

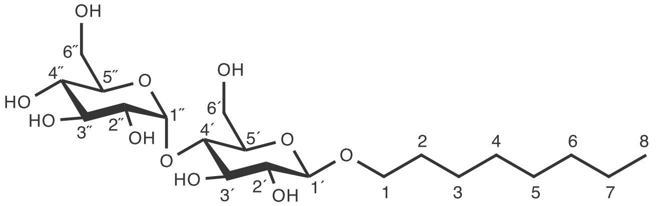

Fig. 1. Chemical structure of the surfactant *n*-octyl-β-D-maltoside (C_8G_2). Carbons 1–8 are in the hydrophobic tail, while carbons 1′–6′ and 1″–6″ are in the hydrophilic head group.

2. Theory

The ^{13}C PT ssNMR spectrum is the sum of resonance lines from magnetically inequivalent ^{13}C sites, each of which being characterized by its ^{13}C chemical shift and linewidth, as well as its efficiency of polarization transfer from the neighboring ^1H. All of these factors have been studied since the inception of solid-state NMR in the 70 s. Based on the extensive previous literature, we have suggested a simplified theory for calculating CP and INEPT intensities as a function of rotational correlation time τ_c and C–H bond order parameter S_{CH} [7]. For the convenience of the reader, we will in the following section briefly summarize the relevant theory for PT ssNMR applied to anisotropic liquid crystals. In addition, we refine our earlier model in order to remedy some deficiencies in the intermediate dynamic regime, and generalize it for molecular segment reorientation that cannot be described with a single correlation time.

2.1. Assumptions

It is challenging and laborious to rigorously treat nuclear relaxation in multi-spin and anisotropic systems [21,22], and in order to make modeling practical we make the following simplifying assumptions already from the outset:

- the effects of relaxation and cross polarization are described with exponential factors,
- the rate constants of these exponential factors are calculated with a random fluctuating fields model,
- at each ^1H and ^{13}C site, the fluctuating field is the non-correlated sum of the fluctuating dipolar fields from neighboring ^1H or ^{13}C nuclei within the same segment, and
- the fluctuating field is isotropic.

Initially, we do not make any explicit assumption on the functional form of the spectral density of the fluctuating field, but rather let it be given by MD simulation trajectories modulated by MAS with the frequency ω_R. The benefit of the model is that it yields physically reasonable predictions (*vide infra*) using a minimum number of free parameters, and thus allows us to focus on the relation between molecular dynamics and the polarization transfer efficiency. Using a more accurate description than the random fields model would lead to significant complication of the mathematics without affecting the qualitative trends that are the main point of this work.

2.2. CP, DP, and INEPT intensities

The CP efficiency is quantified with the signal intensity ratio I_{CP}/I_{DP}^{eq}, where I_{CP} is the CP intensity and I_{DP}^{eq} is the DP intensity for excitation of equilibrium ^{13}C magnetization. The CP process has been rigorously treated with a memory-function formalism [23], which can be modified to take into account the effects of molecular motion and MAS [24–26]. Rather than using the more accurate memory-function approach, I_{CP}/I_{DP}^{eq} is often approximated as [27]

$$\frac{I_{CP}}{I_{DP}^{eq}} = \frac{\gamma_H}{\gamma_C}\frac{\exp\left(-R_{1\rho}^{H}\tau_{CP}\right) - \exp\left(-R_{CH}\tau_{CP}\right)}{1 - R_{1\rho}^{H}/R_{CH}} \quad (1)$$