

Observation of Coupling Across the Ice–Water Interface by 2D Time Domain NMR

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Details about the ice–water interface have application in understanding melting, nucleation, and crystal formation in the pure material as well as in systems involving a solid substrate and water (e.g., hydrated polymers and porous media). This interface has been studied with several techniques including X-ray scattering (1), ellipsometry (2), light scattering (3), and computer simulation approaches (4). Nuclear magnetic resonance is capable of probing dynamics and structure at the molecular level and should be ideally suited for such investigation. Although numerous NMR investigations have been reported involving nonfreezable water in frozen polymer solutions (5) and porous media (6), as well as in certain polycrystalline ice samples (7), any coupling between the ice and water magnetizations was assumed not to contribute to the parameters observed in the NMR experiment. However, if such coupling could be detected, an entirely new avenue for studying the ice–water interface would be available. In this Communication, we report on the first observation of a coupling across this interface.

Proton NMR relaxation measurements were performed at 30 MHz in a 75% H₂O–25% polyethylene glycol (PEG) solution at –25°C. This system consists of polymer, nonfreezable water and ice (8). Figure 1 shows a typical recovery curve obtained using a selective inversion-recovery (9) pulse sequence. This recovery was monitored at a 7 μs time window along the free-induction-decay or transverse decay axis. The multiexponential recovery curve was decomposed into three components using the Marquardt method (10). The spin–lattice relaxation time values and magnitudes of the magnetization fractions are given in the figure legend. At first glance, one would be inclined to associate the long T₁ = 20 s with ice protons and the shorter T₁ values with nonfreezable water and polymer protons. However, as will be shown, such assignment is inaccurate.

To improve the spin-group resolution, a 2D time-domain technique called NMR spin grouping (11) was applied. With this approach, the evolution of the magnetization along both

longitudinal (time τ) and transverse (time t) axes is monitored and analyzed. In a system consisting of several spin groups, this approach makes possible the reconstruction of the lineshape of each spin group from spin–lattice relaxation (T₁) measurements at high field or at low field (T_{1ρ}) using the correlation between the spin–spin relaxation time (T₂) and either T₁ or T_{1ρ}, or both. Figure 2 shows the reconstructed FIDs obtained through spin grouping involving a selective inversion-recovery pulse sequence with 39 τ values and 40 t values. The T₁ values shown in Fig. 2 represent those averaged over all t values.

The three magnetizations, with different T₁ values, each have a liquid-like FID and a solid-like FID associated with

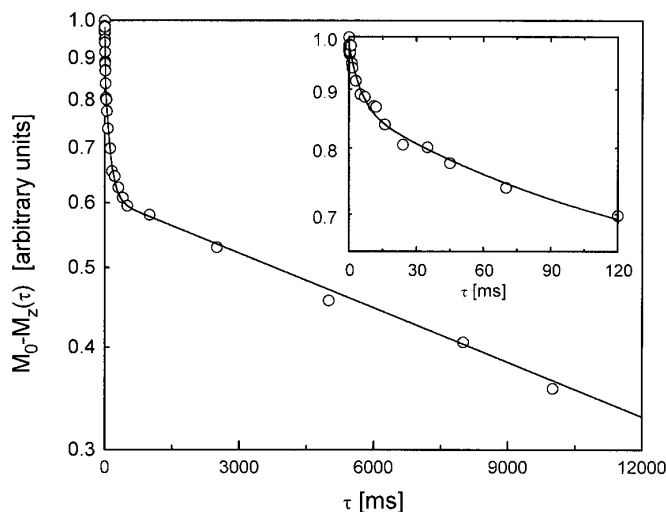


FIG. 1. Magnetization recovery curve obtained at a 7 μs time window using a selective inversion-recovery sequence. A least-squares fit gives

$$\frac{M_0 - M_z(\tau)}{2M_0} = 0.62 \exp\left(-\frac{\tau}{20,000}\right) + 0.27 \exp\left(-\frac{\tau}{110}\right) + 0.11 \exp\left(-\frac{\tau}{5}\right).$$

The inset shows the initial 120 ms of the recovery.

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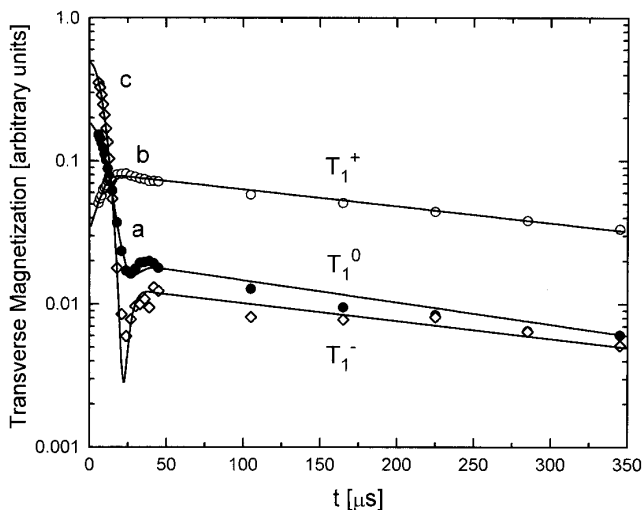


FIG. 2. Reconstructed FIDs obtained from spin-grouping results involving the selective inversion-recovery pulse sequence. $T_1^+ = 5$ ms, $T_1^0 = 110$ ms, and $T_1^- = 20$ s.

it. The liquid-like FIDs can be associated with protons of nonfreezable water. Defining T_2 of the solid signal as the time for this signal to decay to one-half of its initial (at $t = 0$) value, we find that FID a (Fig. 2) has $T_2 = 11 \mu\text{s}$. This T_2 value is the same as that of a sample of dry PEG at -25°C . FID c has $T_2 = 8 \mu\text{s}$ which is the same as for ice at -25°C . A small negative FID b has $T_2 = 8 \mu\text{s}$. The fact that the polymer and nonfreezable water signals as well as the ice and nonfreezable water signals share common T_1 values, taken together with the observation that one of the solid FIDs (FID b) has a negative amplitude, unambiguously indicates that polymer–water–ice magnetization reservoirs are coupled. Although it was known that, in frozen aqueous polymer solutions, the nonfreezable water and polymer protons are coupled, the observation of the ice–water interfacial coupling is new.

The above may be modeled in terms of a three-reservoir magnetization exchange scenario. Letting the reduced longitudinal magnetization for reservoir i be $m_i(\tau) = [M_{0i} - M_i(\tau)]/2M_{0i}$, its evolution with time within the three reservoir exchange scenario may be written

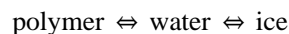
$$\frac{dm_i(\tau)}{d\tau} = -(R_i + k_{ij} + k_{ik})m_i(\tau) + k_{ji}m_j(\tau) + k_{ki}m_k(\tau), \quad [1]$$

where $(i, j, k) = (\text{polymer, water, ice})$, R_i is the intrinsic relaxation rate of the i th reservoir magnetization, and k_{ij} is the rate of magnetization transfer from the i th to the j th reservoir. The solutions of the above coupled differential equations have the form

$$m_i(\tau) = C_i^- e^{-\lambda^-\tau} + C_i^0 e^{-\lambda^0\tau} + C_i^+ e^{-\lambda^+\tau}, \quad [2]$$

where the C_i 's are the apparent magnetization fractions and are functions of the R 's, k 's, intrinsic magnetization fractions, and the effect of the preparation pulse, in the recovery sequence, on the magnetization. Experimentally, the values of C are found from the reconstructed FIDs such as shown in Fig. 2. The λ values are the inverse of the T_1 values shown in Fig. 2.

Details about the intrinsic relaxation parameters (R 's, k 's, and spin reservoir sizes) are obtained by modeling apparent parameters (λ 's and C 's) in terms of the intrinsic parameters. The experimental and modeled apparent parameters are compared within an iterative minimization algorithm, yielding the intrinsic parameters that provide the best match between the two sets of apparent parameters. Performing such exchange modeling on combined results from the above experiment, a nonselective inversion-recovery experiment, and $T_{1\rho}$ experiments at rotating field strengths of 10 G and 2 G yields the high-field relaxation model



with $k_{\text{polymer-water}} = 12 \text{ s}^{-1}$, $k_{\text{water-ice}} = 1 \text{ s}^{-1}$, $(M_0, T_1)_{\text{polymer}} = (21.4\%, 290 \text{ ms})$, $(M_0, T_1)_{\text{water}} = (3.0\%, 10 \text{ ms})$, and $(M_0, T_1)_{\text{ice}} = (75.6\%, 70 \text{ s})$.

It may be noted that the water–ice coupling rate $\sim 1 \text{ s}^{-1}$ is relatively small, but sufficient to mix water–ice magnetizations to some extent on the T_1 time scale and to noticeably reduce the experimentally observed ice proton T_1 .

The fact that the ice–water interfacial coupling can be directly monitored with NMR means that this technique can be utilized to study water molecule coordination and dynamics at this interface. A more detailed report of the present results is in preparation, and a more in-depth NMR study of this interfacial coupling is underway in an ice–water system.

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