Magnetization Transfer in Lamellar Liquid Crystals

Scott D. Swanson[1], and Dariya I. Malyarenko[1]
[1]*Department of Radiology, University of Michigan, Ann Arbor, Michigan, United States*

Introduction: Magnetization transfer (MT) is often used in clinical applications of MRI [1] yet a detailed picture of the underlying physics responsible for MT remains cloudy. Appropriate model systems to study MT will clarify molecular mechanism and help make sense of the MT results collected *in vivo* [1]. Though some work in membrane systems has been done [2], most MT model systems have been either cross-linked proteins (gelatin or albumin) or polysaccharides (agar, agarose, or starch), which are not representative of MT *in vivo*.

Mixtures of surfactants, water, and alcohols form well characterized systems [3,4] that mimic many properties of biological membranes. We have found that these lyotropic lamellar liquid crystals (as surrogate membranes) generate MT between the water and lipid phases and allow numerous molecular permutations to help disentangle MT properties. We report here studies of the mole fraction of decanol and weight percent of water influence on MT parameters, such as the estimated solid component (M^b_0), cross-relaxation rate (R_t), and solid component T2 (T_{2b}), in lamellar liquid crystals composed of sodium dodecyl sulfate (SDS), decanol, and water.

Methods: Based on literature values for lamellar phase [4], known weights of the constituents were added to glass vials. The vials were sealed and then vortexed, centrifuged, heated, cooled, and aged to assure sample uniformity. Care was taken to assure that the samples were in stable regions of the lamellar mesophase [4]. Four samples were made at different weight fractions of water (C_w = 65% and 45%) and different mole fractions (m.f.) of decanol to total lipid protons (decanol + SDS) (χ_c = 0.45 and 0.65). Samples were studied at 22 and 40 °C at 2T. CW RF irradiation (10 sec) was applied at 4 RF power levels and 19 off-resonance frequencies. Data was fitted to the standard MT model using a super-Lorentzian line shape [5] and values of MT parameters were estimated (Fig.1 and Table 1).

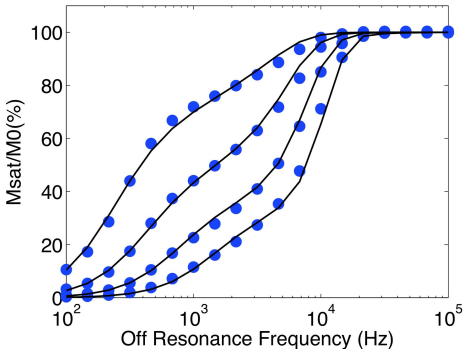

Fig 1. Example of fitting MT model (black lines) to collected data (blue circles). These data are for the sample with C_w = 65% and χ_c = 0.45.

C_w	χ_c	R_a (s^{-1})	R_t (s^{-1})	M^b_0	T_{2b} (μs)
65%	.45	0.59	11.2	0.125	25.1
65%	.65	0.62	6.7	0.217	21.7
45%	.45	0.89	14.3	0.272	23.6
45%	.65	0.92	2.9	0.619	23.3

Table 1. Values of MT parameters estimated in the four samples. Estimated errors are less than 10%.

Results: R_a increases as water content decreases, consistent with a decrease in the average water rotational correlation time. R_t decreases with increased decanol content or conversely increases with increased SDS content. M^b_0 increases with decanol content and with increased lipid (SDS + decanol) content. M^b_0 is discussed at length below. T_{2b} is relatively constant for all four samples but significantly longer than the 10-15 μs typically observed in vivo.

Discussion: Figure 2 shows that, though M^b_0 decreases as water content increases, Fig. 3 confirms that M^b_0 is proportional to the ratio of decanol protons to water protons (additional results from samples at C_w = 65% also plotted). In this chemical system, decanol protons are the primary species participating in MT. A marginal increase in M^b_0 with increasing temperature (not shown), as well as R_t decrease with increasing decanol content likely reflects competition with energy preferred water coordination in sodium hydration sphere. The relatively long value of T_{2b} indicates significant motion within semi-solid part of the liquid crystal. This motion will minimize intermolecular NOE (between decanol and SDS) and quench spin diffusion. This scenario is fortified by MT studies of lamellar samples prepared in D_2O. In the deuterated samples, we easily see the lipid proton NMR signal and find that the lineshape is due to inhomogeneous broadening: off-resonance RF saturation does not uniformly decrease the intensity of the lipid resonance.

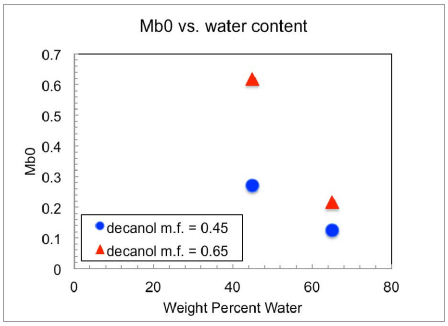

Fig. 2. M^b_0 plotted as a function of weight percent water (C_w). Though M^b_0 does decrease as water content increases, the decanol content of the lipid phase also contributes to the estimated value of M^b_0.

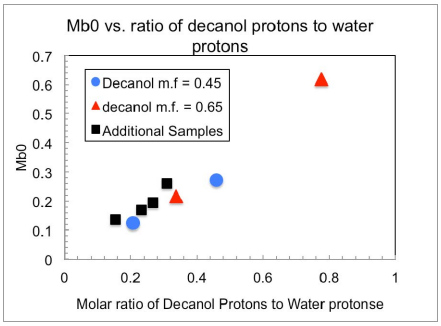

Fig. 3. M^b_0 plotted as a function of the molar ratio of decanol protons to water protons. These data indicate that M^b_0 is determined primarily by the amount of decanol in the sample and that MT occurs predominantly between water and decanol.

Conclusions: Lyotropic liquid samples provide a convenient model to study the molecular properties of MT representative of in vivo systems. The ability to observe the solid-like fraction, control over the water content, control over the molecular constituents and the ability to selectively deuterate individual molecular species will lead to a more complete molecular picture of MT. The composition of biological membranes *in vivo* may affect the amount of MT generated.

References: [1] Stanisz G, et al. Magn. Res. Med. 2005; 54:507-512. [2] Kucharczyk W, et al. Radiology. 1994;192(2):521-9. [3] Quist PO, Halle B, Furo I. JChem. Phys. 1991;95(9):6945-61. [4] Berger K, Hiltrop K. Coll.Polym. Sci. 1996;274(3):269-78. [5] Henkelman RM, et al. Magn. Res. Med. 1993;29(6):759-66.