Lanthanide complexes with lipids as nonlinear NMR sensors of the local temperature due to both paramagnetic lanthanide-induced shifts and relaxation rates

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NMR techniques have previously been used to determine the physical and chemical properties of paramagnetic lanthanide (Ln) compounds in "pure" homogeneous aqueous and organic solutions {these systems are characterized by a linear dependence of paramagnetic lan-thanide-induced shifts (LISs, ΔδLIS) on 1/T} [1]. In this study, we investigated the temperature dependences of paramagnetic lanthanide-induced shifts (LISs, ΔδLIS) and of the transverse relaxation rate enhancements (TRRE, R2) of signals in such a heterogeneous medium as liposomes {in complex systems of phospholipids POPC, DPPC, DMPC, and DOPC with Ln cations}. It has been established by NMR that the dependence of LIS on 1/T is conditionally fragmented into several segments with different slope angles (which corresponds to the reorganization of the structure of the complexes due to phase transitions in micelles). The results obtained indicate that Ln complexes with phospholipids can be used as tunable nonlinear temperature-sensitive probes for local temperature determination and advanced disease diagnostics using NMR/MRI “shifting” technologies [2].

Temperature dependence of the TRRE was measured using the examples of unsaturated POPC lipid and saturated DPPC and DMPC lipids. It was demonstrated that for unsaturated POPC lipid viscosity is do not depend on the temperature. In addition, for DPPC and DMPC lipids viscosity do not depend on the temperature below phase transition temperature, but near the phase transition temperature dramatic increase of the viscosity was observed {ac-cording to the Curie-spin contribution to the paramagnetic TRRE}. Obtained results show that Ln-phospholipid complexes could be used as nonlinear sensors for determining local viscosity and temperature of lipid membrane using NMR/MRI relaxational technologies.

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