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Title:	Structural and dynamical aspects of PEG/LiClO ₄ in solvent mixtures via NMR spectroscopy
Authors:	Singh, Satnam (/jspui/browse?type=author&value=Singh%2C+Satnam) Dorai, K. (/jspui/browse?type=author&value=Dorai%2C+K.)
Keywords:	Polyethylene glycol Molecular weights Hydrodynamic structure
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Abstract:	Motivated by the potential usefulness of polyethylene glycol (PEG)/Li ⁺ salt mixtures in several industrial applications, we investigated the structure and dynamics of PEG/LiClO ₄ mixtures in D ₂ O and its mixtures with CD ₃ CN and DMSO-d ₆ , in a series of PEG-based polymers with a wide variation in their molecular weights. ¹ H NMR chemical shifts, T ₁ /T ₂ relaxation rates, pulsed-field gradient NMR diffusion experiments, and 2D HOESY NMR studies have been performed to understand the structural and dynamical aspects of these mixtures. Increasing the temperature of the medium results in a significant perturbation in the H-bonded structure of PEG in its PEG/LiClO ₄ /D ₂ O mixtures as observed from the increase in chemical shifts. On the other hand, the addition of molecular cosolvents has a negligible effect. The hydrodynamic structure of PEG shows a pronounced variation at low temperature with increasing molecular weight, which, however, disappears at higher temperatures. Increasing the temperature leads to a decrease in the hydrodynamic structure of PEG, which can be explained on the basis of solvation-desolvation phenomena. The 2D HOESY NMR spectra reveal a new finding of Li ⁺ -water binding in the PEG/LiClO ₄ /D ₂ O mixtures with the addition of molecular solvents, suggesting that the Li ⁺ cation diffuses freely in the D ₂ O mixtures of polymers as compared with the polymer mixtures with DMSO or CD ₃ CN.
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