Solvation Dynamics of Concentrated Aqueous Polymer Mixtures: A Two-Dimensional Infrared Spectroscopy Study

Kimberly R. Daley and Kevin J. Kubarych*
Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, MI 48109, USA
kubarych@umich.edu*

Two-dimensional infrared spectroscopy is used to explore the chemical dynamics of crowded polymer mixtures. Using a transition metal carbonyl probe in solution, we find unexpected polymer length and concentration dependent dynamics in D_2O.

Understanding crowded polymer solutions is a significant open challenge that has received little attention using modern spectroscopic techniques, like 2DIR. We use two-dimensional infrared spectroscopy (2DIR) to explore the solvation dynamics of increasing concentrations and increasing lengths of poly(ethylene) glycol (PEG) in D_2O solution. We investigate how structural properties influence the hydration dynamics and how water behaves as polymer chains begin to overlap and entangle. We are particularly interested in determining how water responds to being crowded by macromolecules, of which PEG is a prototype case. In crowded environments, the molecules may behave different than they do in the idealized dilute solutions of conventional chemical models. Studying the fundamental properties of polymer mixtures has implications in understanding biologically relevant heterogeneous mixtures, such as blood, as well as other applications, such as solution polymer processing, heterogeneous catalysis, hydraulic fracturing, microfluidic technology, biochemical studies, and biophysical studies [1-3]. Our studies can provide fundamental information about the hydration dynamics of crowded polymer solutions, such as how to link molecular properties of friction to macroscopic properties of viscosity. By studying the fundamental properties of these mixtures, we learn how crowding and confinement affects the structural and dynamical properties of liquids on both a micro- and a macro-scale. Previous work has investigated the protein and hydration dynamics of crowded hen egg white lysozyme labeled with a metal carbonyl molecule [4]. The results indicated a non-linear dynamical transition in hydration dynamics induced by macromolecular crowding. This current work details the dynamics of the metal carbonyl CORM-2B, which is derived from a carbon-monoxide releasing molecule (CORM-2). CORM-2B is crowded with PEG at varying lengths, and surprisingly we find that for long PEGs with molecular weight (mw) greater than ~400 Dalton, we find bulk water dynamics, even in concentrated solutions. In contrast, we do find concentration dependent dynamics in low-mw PEG. These results provide an interesting window into the nature of polymer solutions, which are characterized alternatively using simple coarse-grained treatments and molecular descriptions.

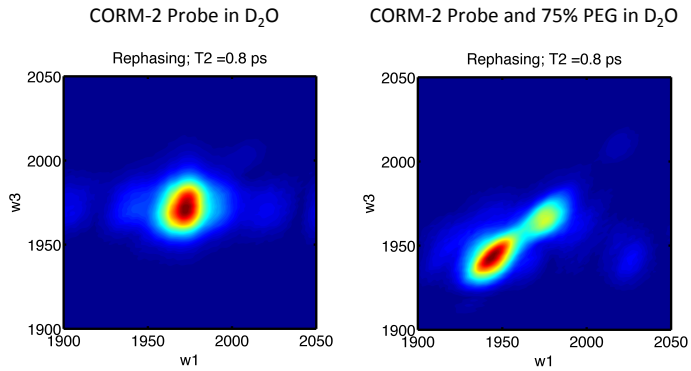

Figure 1. 2DIR Spectra of CORM-2B and 75% PEG by volume.

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