

Rotational dynamics of solutes with multi-rotational axes in 1-alcohol solutions studied by infrared pump-probe spectroscopy

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We observed the anisotropy decays of N₃ derivatized amino acids in the primary 1-alcohols with infrared pump-probe spectroscopy. From the temperature dependence of the rotational relaxation time, it is suggested that there are some correlations between rotational motions of the azide group and the nearby alkyl chain.

So far, we have investigated the rotational dynamics of unnatural amino acids, which have the N₃ groups as vibrational probes, in water with infrared (IR) pump-probe spectroscopy [1]. Reflecting the structural difference around the N₃ group, the observed anisotropy of the solutes showed different decaying behaviors; as the structural freedom around the vibrational probe increases, the decay becomes faster. According to the results, we have suggested that the rotational motion of the N₃ group has some correlations with that of the alkyl chain neighboring to the vibrational probe in the aqueous solution. The knowledge of the rotational dynamics of the solute with multi-rotational axes must be essential to understand the structural dynamics of macromolecules, such as proteins. In this study, we chose three different azide-derivatized amino acids (N₃-Ala, N₃-Pro and N₃-Nle) as solutes, and primary 1-alcohols (CH₃(CH₂)_nOH, n = 0 - 3) as solvents. We performed IR pump-probe measurements for these molecules in each alcohol, and in 1-BtOH at different temperatures from 283 K to 333 K. Because each of them has the different structural flexibility around the N₃ group, from the viscosity and temperature dependence of their rotational dynamics, we will be able to obtain the detailed information on the relationship between rotational motion of N₃ group and the other rotational modes. Figure 1 describes the anisotropy decays of N₃-Nle in 1-BtOH measured at different temperatures. These decay curves can be characterized by a double-exponential function with sub-picosecond and picosecond time constants, which considered to be reflect the thermal fluctuations and rotational dynamics of the N₃ group in 1-BtOH, respectively. Including the results for N₃-Ala and N₃-Nle in 1-BtOH, we show the obtained fast and slow rotational relaxation times in Fig. 2. As shown in Fig. 2, although the fast time constants depend only on temperature, the slow ones not only on temperature but also on the solute. Based on the Stokes-Einstein-Debye theory, the temperature dependence of the slow time constants indicates that, as the structural freedom around the N₃ group increases, the effective hydrodynamic volume of the N₃ group in 1-BtOH becomes smaller due to the correlated rotational motion of N₃ group and the neighboring alkyl chains.

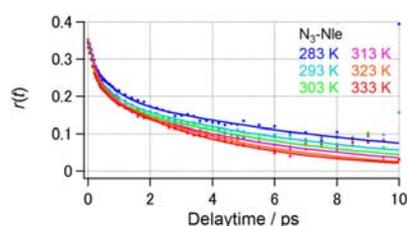


Figure 1. Anisotropy decays of N₃-Nle in 1-BtOH measured at different temperatures. Solid line indicates the fitting result.

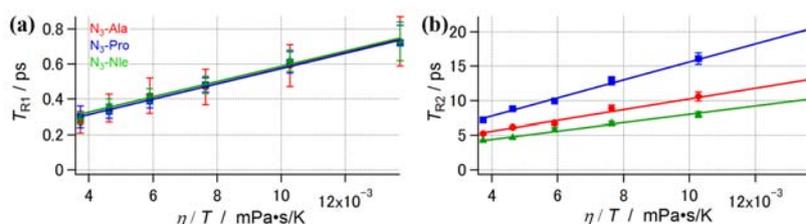


Figure 2. Temperature dependence of (a) fast and (b) slow time constants of (red) N₃-Ala, (blue) N₃-Pro and (green) N₃-Nle. Solid line represents the fitting result with a linear function.