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## **Molecular free volume and viscosity changes in non-Newtonian fluids probed with molecular rotors**

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An empirical relationship between molecular free volume and viscosity has been established (Doolittle AK, *J Appl. Phys.* 1952; 23: 236-9). Non-Newtonian fluids hold much importance to scientific study because of their ubiquity in nature - from gelatins to starches to blood. The purpose of this study was to examine the relationship between molecular free volume and viscosity in non-Newtonian fluids under shear-thinning conditions. Molecular rotors are fluorescent probes for free volume. After photoexcitation, these molecules can decay from their singlet state either through radiation (fluorescence) or torsional relaxation (intramolecular rotation). In environments with low free volume, intramolecular rotation is hindered, and the radiative deexcitation pathway becomes dominant. This behavior is accompanied by a measurable increase in fluorescence intensity. Molecular rotors have been used successfully as viscosity probes in various fluids and polymers. Two molecular rotors, CCVJ (9-(2-carboxy-2-cyano)-vinyl-julolidine) and CCVJ-TEG (CCVJ-triethyleneglycol ester), were dissolved at 10 $\mu$ M in an aqueous solution of KelcoGelf (gellan gum) and subjected to shear forces both in a tube shear apparatus for fluorescence measurements and in a Haake VT-550 rheometer to determine the shear-thinning behavior. The gellan solution exhibited power-law behavior with an exponent  $n=0.48$ . In spite of this strong shear-thinning behavior, no change in rotor emission intensity was observed. Additionally, a novel behavior of some molecular rotors, a sensitivity towards fluid flow (Haidekker MA et al, *Sensor Lett.* 2005; 3: 42-8), was exploited to observe shear-thinning behavior by probing flow velocity in a tube. Under application of sufficiently high shear rates to cause shear thinning, molecular rotors revealed no change in free volume as observed with fluorescence intensity. This preliminary study suggests that molecular free volume and shear thinning are independent properties. Further studies will be needed to corroborate that the free volume of a fluid is not related to its viscosity in shear-thinning environments.