STRUCTURAL FLUCTUATIONS IN AN AZEOTROPE: UNDERSTANDING THE BENZENE-METHANOL AZEOTROPE

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The structure and dynamics of molecular liquids and their binary mixtures have been of interest for a long time. Azeotropes is a particular class of liquid mixture that boils at a constant temperature at a specific composition. Understanding of azeotropic systems at the molecular level is limited. In this study, we try to investigate this azeotropic non-ideality, using ultrafast Optical Kerr Effect (OKE) spectroscopy, broadband (1-10 THz) THz-Time domain spectroscopy (THz-TDS) along with temperature-dependent Nuclear Magnetic Resonance spectroscopy (NMR) of the azeotropic as well as mixtures of different compositions of benzene and methanol.

Vibrational and NMR spectroscopic studies show that the formation of the methanol-benzene azeotrope weakens the hydrogen bond network. Intermolecular forces between the benzene molecules are also reduced significantly. Methanol disrupts the stacking in benzene which is also evident from the depression in the boiling points. Ultrafast OKE spectroscopy is a powerful tool to probe both, the collective orientational diffusion and the intermolecular dynamics in liquids. The spectral density (SD) obtained by the Fourier deconvolution of the OKE time transients gives us information about the structural relaxation occurring in the liquid at the terahertz and sub terahertz frequencies. With the increase of methanol in the mixtures, the α relaxation timescales become faster. An azeotropic composition mixture was prepared at room temperature without further distillation. The spectral densities of this mixture and the azeotrope at frequencies pertaining to collective intermolecular dynamics were quite different from each other. All of benzene's entire rotational dynamics show up as molecular reorientation having contributions throughout the OKE spectra. The centre-of-mass translational part is only visible when it affects the interaction induced (I-I) part of the polarizability[a]. The addition of methanol decreases this contribution of the translations to the I-I term for benzene. A detailed analysis of the similarity of the azeotrope spectral density to benzene and how they differ from the other composition mixtures can give us useful insights into the structural fluctuations happening in the picosecond timescales in the benzene-methanol mixtures.

[a]Ryu, S.; Stratt, R. M. J. Phys. Chem. B 2004, 108, 6782.