An electrospray technique for the study of liquid energetics by hyperquenched glass calorimetry

Li-Min Wang, * Steve Borick, # and C. Austen Angell *
* Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604
# Department of Chemistry, Scottsdale Community College, Scottsdale, AZ 85256

ABSTRACT

We describe an electrospray technique for in situ preparation, for differential scanning calorimetry study, of samples of molecular liquids quenched into the glassy state on extremely short time scales (hyperquenched). We study the case of a hydrogen bonded liquid, propylene glycol, PG and a Van der Waals liquid, dibutyl phthalate. Using a fictive temperature method of obtaining the temperature dependence of enthalpy relaxation, we show that the electrospray method yields quenching rates of \(~10^5\) K/s, while the more common method, dropping a sealed pan of sample into liquid nitrogen, yields only 120 K/s. These hyperquenched samples start to relax, exothermically, far below the glass temperature, at a temperature (\(0.75T_g\)) where the thermal energy permits escape from the shallow traps in which the system becomes localized during hyperquenching. This permits estimation of the trap depths, which are then compared with the activation energy estimated from the fictive temperature of the glass and the relaxation time at the fictive temperature. The trap depth in molar energy units is compared with the "height of the landscape" for PG, the quasi-lattice energy of the liquid based on the enthalpy of vaporization, and the single molecule activation energy for diffusion in crystals. The findings are consistent with the mechanism of relaxation invoked in a current model of relaxation in glassforming liquids.

Keywords: Glass transition, structural relaxation of liquids and glasses, Fragility of liquid, Differential scanning calorimetry.

Author to whom correspondence should be addressed: Dr. C. Austen. Angell, caa@asu.edu