22. Viscosity and diffusion in supercooled glycerol-water mixtures

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The viscosity of supercooled glycerol aqueous solutions, with glycerol mass fractions between 0.70 and 0.90, have been determined to confirm that the Avramov-Milchev equation describes very well the temperature dependence of the viscosity of the binary mixtures including the supercooled regime. Chronoamperometric measurements with cylindrical microelectrodes were also used to investigate the diffusion of ferrocene methanol in super-cooled glycerol aqueous solutions over a wide range of viscosity (1.5×10^{-3} – 1.5×10^{2} Pa.s) and reduced temperature ($0.50 < T_g/T < 0.78$). Diffusion-viscosity decoupling was observed at $T_g/T \approx 0.65$, being the diffusion coefficient of the probe close to the glass transition temperature much higher than that predicted by the hydrodynamic Stokes-Einstein model. Contrary to the observed dependence on concentration of the reduced temperature onset of the decoupling for the diffusion of glycerol in glycerol-water mixtures, the onset of the decoupling of ferrocene methanol in the same mixtures seems to be independent on the mixture composition. A critical analysis of the viscosity data of the mixtures in the supercooled region allowed us to reconcile both results.