Liquid mixtures involving fluorinated alcohols: The equation of state (*p, r, T, x*) of (Ethanol + Trifluoroethanol) Experimental and Simulation

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Fluorinated alcohols are substances with unique properties and high technological value in the pharmaceutical and chemical industries. Trifluoroethanol (TFE), in particular, displays a number of unusual properties as a solvent. For example, it dissolves nylon at room temperature and is effectively used as solvent in bioengineering. The presence of the three fluorines atoms gives the alcohol a high ionization constant, strong hydrogen bonding capability and stability at high temperatures.

In the pharmaceutical industry, TFE finds use as the major raw material for the production of inhalation anesthetics. Mixtures of TFE and water (known as Fluorinols®) are used as working fluids for Rankine cycle heat engines for terrestrial and space applications, as a result of a unique combination of physical and thermodynamic properties such as high thermal efficiency and excellent turbine expansion characteristics.

Environmentally, TFE is a CFC substitute with an acceptable short lifetime and with small ozone depletion potential. Additionally, TFE is known to induce conformational changes in proteins and it is used as a co-solvent to analyze structural features of partially folded states.

The (ethanol + TFE) system displays an interesting and peculiar behaviour, combining a negative azeotrope with high positive excess volumes.

In this work, liquid mixtures of (ethanol + TFE) were investigated. The densities of the mixtures were measured as a function of composition between 278K and 338K and at pressures up to 700 bar. The corresponding excess volumes as a function of temperature and pressure, the isothermal compressibilities and thermal expansivities were calculated from the experimental results. The mixtures are highly non-ideal with excess volumes ranging from 0.8 - 1.0 cm^3mol^{-1}.

Finally, molecular dynamic simulations were performed to model and interpret the experimental results. The Trappe force field was used to simulate the (TFE + ethanol) mixtures and calculate the corresponding excess volumes. The simulation results are able to reproduce the correct sign and order of magnitude of the experimental VE without fitting to the experimental data. Furthermore, the simulations suggest the presence of a particular type of hydrogen bridge between ethanol and TFE, that can help to rationalize the experimental results.