Fluid Phase Behavior of (Ionic Liquid + Alcohol) Binary Mixtures: 1-Hexyl-3-Methylimidazolium Bistrisflamide + C2-C8 N-Alcohols

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In this work we present results of fluid phase equilibria of (ionic liquid-alcohol) binary mixtures in the temperature range $260 < T/K < 340$ and pressures up to 500 bar, as well as orthobaric excess volumes for the same mixtures at $298 < T/K < 333$. The ionic liquid chosen was the 1-hexyl-3-methylimidazolium bistrisflamide, [C6mim][NTf2], and the alcohols were linear with the alkyl chain ranging from C2 to C8. These studies involving the liquid-liquid equilibrium behavior and volumetric properties of mixtures can have a double objective: i) they can supply data which are required for mass balance and mass transfer calculations in phase separation processes and ii) they can provide some insight about the nature of the interactions between the ionic liquid's ions and solvent molecules.

Some liquid–liquid equilibrium temperatures at 0.1 MPa nominal pressure were determined using a dynamic method with visual detection of the phase transitions. Temperature was measured using a PRT coupled to a Keithley 199 System DMM/Scanner. The thermometer was calibrated against high accuracy mercury thermometers (± 0.01 K). The effect of pressure on the phase diagrams was obtained by a laser light scattering technique. The apparatus uses a stainless steel cylindrical cell closed on both sides with thick sapphire windows. It was used for experiments where pressure was raised up to 500 bar. In the case of isothermal runs, cloud-point temperature accuracy is maintained (±0.01 K) but it worsens a bit for isobaric runs. As for pressure, the uncertainty is ±1 bar in this higher-pressure range.

The phase diagrams obtained only show UCST branches. The miscibility of each alcohol in the [C6mim][NTf2] decreases with the increase in the alcohol chain length. As for pressure effects, the miscibility improves upon pressurization for butanol (negative slope of the T–p plot) but worsens for hexanol (positive slope of the T–p plot). This type of behavior at the UCST usually denotes that mixtures are formed upon contraction for butanol (excess volume, $VE<0$), and expansion for hexanol (excess volume, $VE>0$), because under some common restrictive assumptions, this constitutes a thermodynamic requirement.

Atmospheric pressure density measurements were performed in an Anton-Paar DMA 5000 vibrating-tube densimeter with temperature stability better than 0.005 K. Judging from the repeatability of the results, the estimated uncertainty of the VE results are typically ± 0.03 cm^3 mol^{-1}.

Irrespective of the nature of the mixture (the size of the alcohol alkyl chain), all excess molar volumes are small (of the order of tenths of cm^3 mol^{-1} — less than 0.1% of the mixture's molar volume). It was also found that the VE values for these liquid mixtures are basically insensitive to temperature. A more peculiar feature of the curves is their asymmetry and, in some cases, their sign inversion. The most relevant result is that at the critical concentration the VE obtained for butanol and pentanol are in close agreement with what was expected from the measured dT/dp of the liquid-liquid consolute curve.

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