Do Thermophysical Properties Support the Percolation Model in Ionic Liquids?

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Ionic liquids are nanostructured fluids in which the ion pairs arrange themselves into polar and nonpolar domains. The structural segregation in these systems will depend on the size of the polar and nonpolar regions in each ion, which may exist as dispersed or continuous microphases. The transition between these two phases is related with the percolation phenomenon, and depends on the relative size of the high-charge and low-charge regions in each ion and the size of the alkyl chain length. If the thermophysical data is obtained with enough resolution and/or accuracy, the percolation phenomenon in ionic liquids should be reflected somewhere in the trend of the thermophysical properties. In order to explore and find some experimental support for the percolation model, a set of basic thermophysical properties and their temperature dependency (vapor pressures, enthalpies and entropies of vaporization, viscosity, surface tension, refraction index, heat capacities) were measured and evaluated for families of NTf₂ based ionic liquids. The resolution and accuracy of the obtained results allowed the observation of a trend shift along the alkyl chain length and a subtle odd-even effect related with a structural change, in agreement with the percolation model. In this talk, some improvements of the Knudsen effusion apparatus, in order to obtain suitable vapor pressure results of ionic liquids, will be presented. The obtained results for an extended number of imidazolium and pyridinium bis(trifluoromethylsulfonyl)imide were used to dissect reliable enthalpic and entropic contributions to the vaporization equilibrium. The thermodynamic properties of vaporization together with other selected thermophysical properties will be used to establish the bridge between the thermodynamic trend and structural effects (alkyl chain length and molecular symmetry), enabling some experimental insights concerning the percolation phenomenon in ILs and their impact on the thermophysical properties.