The Complex Structure of Ionic Liquids Probed by Molecular Dynamics Simulation

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The concept that the structure of ionic liquids is complex and can exhibit nano-scale segregation started to be investigated almost ten years ago via molecular modeling. A systematic molecular dynamics study has been performed in order to extend the analysis of the mesoscopic segregation behavior observed in different ionic liquids. The analyses include the discussion of the structure factors, *S(q)*, in the low-*q* range ($1.6 \leq q\ nm^{-1} \leq 2.0$); the confirmation of the periodicity of the polar network of the ionic liquid and its relation to the so-called intermediate peaks; and the characterization of the polar network and the nonpolar regions that are formed along the series using aggregate analyses by means of five different statistical tools. The analyses confirmed that the percolation of the nonpolar regions into a continuous domain can occurs but that this is not a sufficient condition for the emergence of a distinct and intense prepeak. The lowest-*q* peaks of the structure factor spectra (prepeaks) can be assigned to characteristic separations between strands of the ionic liquid polar network that are mediated by nonpolar regions. On the other hand, the second lowest-*q* peaks reflect the medium-range ordering of the polar network itself. Finally, the systematic comparison between different groups of ionic liquids allows us to rationalize the relative amplitude and position of those peaks with the underlying structure of the ionic liquid and interpret such an outcome in terms of the relative size and nature of the corresponding ions.