

**RELATIONSHIPS BETWEEN THE STRUCTURE, NANOSTRUCTURE,
AND PROPERTIES OF IONIC LIQUIDS***Sedov I.A.*Kazan Federal University
420008, Kazan, Kremlevskaya Str., 18

Many ionic liquids (ILs) exhibit a distinct nanoheterogeneous structure, composed of interpenetrating polar and apolar domains. Nanoheterogeneity is particularly prominent in ILs with longer alkyl chain lengths, which form large apolar domains. Domain segregation can be identified using experimental scattering techniques or from molecular dynamics simulations. However, there is no straightforward way to quantify nanoheterogeneity. The scattering peak position only provides an average length scale for both polar and apolar domains. When analyzing instantaneous configurations from computer simulations, the percolating sponge-like geometry of the domains makes it difficult to isolate apolar or polar atom clusters and measure their size.

In this work, the chord length distribution method was applied for the first time to the analysis of domain structure in different ILs. We define an apolar domain as all the points of space inside the simulation cell that are closer to the polar than to any apolar heavy atom in the liquid. In a polar domain, all the points lie closer to a polar atom. Hence, these domains consist of Voronoi cells around apolar or polar atoms. Random lines are then generated and the lengths of the line segments cut by the boundaries of the polar and apolar domains are determined. The distribution of these segment lengths characterizes the sizes and shapes of the clusters of apolar and polar atoms.

Molecular dynamics simulations of ILs were conducted at 298 K in the NPT ensemble using the OPLS force field in large cells containing 4000 ion pairs. The simulation results were validated by comparing the predicted and experimental SAXS curves. The instantaneous configurations were analyzed using a program written by the author.

The results of analysis revealed a number of interesting relationships between the structure of the cation and the nanostructure of the IL. Alkylammonium ILs with the same number of alkyl groups (mono-, di- or tri-) but with different alkyl chain size show very similar distributions of chord lengths in the polar domain. The size of clusters in the apolar domain grows up with increasing number of carbons in the alkyl group. At the same time, cations with different numbers of the same substituents (e.g. mono-, di- and tributylammonium) have almost the same structure of apolar domains and strikingly different polar domains. While polar atoms tend to aggregate in monoalkylammonium salts, their distribution is much closer to uniform in di- and especially trialkylammonium ILs. Similarly, imidazolium ILs with two identical alkyl substituents and those with one such substituent form apolar clusters of the same size. The nature of the IL anion also affects domain segregation. Large anions can impede apolar aggregation.

The nanostructure of ILs strongly influences their properties. This is shown by the example of solvation properties using experimental free energies of solvation and calculated free energies of cavity formation, which depend on the cluster size distribution.

The work was supported by RSF project №24-13-00062.