The structure of ionic liquids in terms of intermolecular voids

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The all-atom and coarse-grained MD models of a number of ionic liquids (ILs) are studied. The modern MD models make it possible to reliably reproduce existing experimental data. However, the main value of MD modeling is that it gives the coordinates of the atoms of the simulated system, which makes it possible to study the structural features of solutions that cannot be extracted from the experiment. In our work the special attention is paid to the analysis of intermolecular voids. The Voronoi-Delaunay method is used, with the help of which it is possible to calculate the empty volumes related to different components of the system: anions, cations (separately to their heads and alkyl tails) and dissolved gas molecules, as well as to select and estimate the sizes of real interatomic voids. The distributions of radii of the interstitial spheres are studied, separately for the entire ionic liquid and for its components with charges of different signs. A conclusion is made about specific spatial correlations of anions and cations [1]. For comparison, models of the same mixtures were obtained at the same density, but without charges on the molecules. A significant difference is shown in the mutual arrangement of molecules corresponding to anions and cations. It turns out that for the system considered as a whole, the interatomic voids are the same for the ionic liquid and its neutral analog. This means that the spatial distribution of molecules is determined mainly by the impermeability of atoms, while electrostatic interactions dictate only the features of the mutual arrangement of components within a given spatial distribution [2]. Models of ILs with gas molecules dissolved in them are calculated and studied [3]. The empty volumes related to different components of ionic liquids are found, it is shown that the regions of alkyl substituents are the loosest. It is also shown that gas molecules contribute an additional empty volume, which is localized exclusively in their nearest environment.

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