STRUCTURE AND THERMODYNAMICS OF WATER-DIOXANE MIXTURES BASED ON MOLECULAR DYNAMICS SIMULATION

Ved'kal A.V.[(1,2)], *Kadtsyn E.D.*[(1,2,3)]
[(1)] SRF "SKIF"
630559, Koltsovo, Nikolskiy pr., 1
[(2)] Novosibirsk State University
630090, Novosibirsk, Pirogova st., 2
[(3)] Voevodksy Institute of Chemical Kinetics and Combustion, SB RAS
630090, Novosibirsk, Institutskaya st., 3

Thermodynamic data are often used to insight into molecular processes. It is usual to fit such parameters as molecular interaction energy or molecular complexes' structure to reproduce observed macroscopic values of enthalpy, heat capacity etc. Structural experiments like X-ray diffraction, SAXS or WAXS measurements can support or deny the chosen model. Currently, computer simulation tools such as molecular dynamics (MD) help one to combine structural and thermodynamic approaches together. In MD model all atomic coordinates in the system are known in every moment, so the model can be directly compared with structural data and explain the experimental observations. Because details of molecular interactions are also known for MD model, one can directly extract the thermodynamics data.

In the work we show the advantage of MD simulation for understanding experimental findings on the example of water-dioxane mixture study. Atomic pair correlation functions were compared with experimental SAXS data on the whole range of concentrations. Structure factors were calculated. Analysis of partial g(r) and S(q) for individual components gives better explanation of experimental data, where only total scattering on the all system atoms can be measured. Analysis showed that mixture is highly heterogeneous in the middle concentration range, with spanning clusters of water molecules formed. The fact explains the very slow changes of thermodynamics parameters, such as partial enthalpies, in these concentrations.

Analysis of hydrogen bonds support also showed slow change in the middle concentrations with high number of water-water bonds, what support the suggested structure. Additional analysis of intrinsic volumes also supported the picture and explained features of solution volumetric parameters, namely a minimum on the water partial volume.

The work underlined the fruitfulness of MD simulation in understanding structural and thermodynamics data and refining the structural model.

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