NEW VOLUMETRIC CHARACTERISTIC FOR SOLUTION THERMODYNAMICS

Kadtsyn E.D.(1,2,3), *Koshelev L.D.*(1,2), *Ved'kal A.V.*(2,3), *Nichiporenko V.A.*(2), *Medvedev N.N.*(1,2)

(1) Voevodksy Institute of Chemical Kinetics and Combustion SB RAS
630090, Novosibirsk, Institutskaya st., 3
(2) Novosibirsk State University
630090, Novosibirsk, Pirogova st., 2
(3) SRF "SKIF"
630559, Kol\`tsovo, Nikol\`skiy prospect, 1

We introduce new solution volumetric characteristics (components' intrinsic molar volumes) which are real volumes assigned to solution components. Under real component volume we mean the part of space which is naturally inherent to it and include both component's molecules as well as parts of intermolecular voids being closer to that component's molecules that to other molecules. New characteristics differs fundamentally from known partial volumes which are just solution volume derivatives by components amount and do not reflect real volumes.

A theoretical meaning of new characteristics is that they are connected by rigid equations with observed parameters such as excess volume, components' partial volumes etc. It is important, that real volumes of molecules are determined by their arrangement. The new characteristics can hence relate solution molecular structure with its thermodynamic parameters.

Intrinsic volumes we have proposed to use are unable to measure in real experiments. It is possible however to obtain them in molecular-dynamic model. Having coordinates of all atoms given one is able to calculate real volume of each molecule with aid of Voronoi tessellation and establish components intrinsic volumes behavior in dependence of concentration. As a result, we can give a structural interpretation of observed macroscopic solution properties: we explain the presence of extrema on partial molar volumes of alcohols in solution [1]; we also explain the nature of negative excess volume in aqueous solutions of nonelectrolytes on the molecular level.

1. Nichiporenko V.A., Kadtsyn E.D., Medvedev N.N., J. Mol. Liq., 2025, 423, 127005

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (FWGF-2021-0002) and also partially within the governmental order for SRF ""SKIF"" Boreskov Institute of Catalysis (FWUR-2024-0040).