

Voronoi analysis of solutions volumetric properties

Evgenii D. Kadtsyn,^{1,2*} Vladislav A. Nichiporenko^{1,2}

¹ Natural Science department, Novosibirsk State University, Pirogova 1, 630090, Novosibirsk, Russia

² Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Institutskaya 3, 630090, Novosibirsk, Russia

* E-mail: e.kadtsyn@q.nsu.ru.

Volumetric properties are thermodynamic properties calculated from system density like partial molar volume. They are often used in solution chemistry to investigate solution structure. Their concentration behavior and its possible features can shed light on molecular processes occurring in solution. On the other hand, volumetric properties are thermodynamic characteristics which have no direct geometrical sense (except the total system volume). That makes their structural interpretation rather speculative. To draw structural conclusions relation between volumetric properties and microscopic molecular volumes are highly desirable.

In our previous works, such relations were derived. We introduced the concept of component Voronoi molar volume, which is the mean value of Voronoi volume of component molecules in a solution. We expressed solution volumetric properties via components Voronoi molar volumes. Our expressions allow us to analyze volumetric properties from molecular volumes' point of view. It is possible to consider solute and solvent contributions to properties separately and search for reasons for appearing the features like partial volume minima.

In the present work, our approach was expanded to aqueous alcohol solutions. Molecular dynamics models of methanol, ethanol, 1- and 2-propanols were obtained, and Voronoi tessellation was performed. Components' Voronoi molar volumes were shown to decrease over the whole concentration range studied. Alcohols' partial molar volumes were evaluated, and all of them have a minimum at small concentrations. Analysis of separate contributions revealed their reason connected with the finishing of water volume decrease.

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[2] E.D. Kadtsyn, V.A. Nichiporenko, N.N. Medvedev, *Journal of Structural Chemistry* **2021**, 62 (1), pp. 61-72 (In Russian).