Quasichemical Models of Structure and Physicochemical Properties of 1,4-Dioxane-Methanol and 1,4-Dioxane-Ethanol Mixtures

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Recently developed unified approach to describe a number of physicochemical properties of solutions on the basis of quasichemical models opens up new possibilities in study of association and solvation and macroscopic manifestations of supramolecular organization in properties of liquid mixtures [1-3]. Considered in the report are results on study of association and solvation processes in the binary mixtures of 1,4-dioxane with methanol and ethanol and description of their thermodynamic and dielectric properties. The binary mixtures of 1,4-dioxane with alcohol present the solutions of polar associating solute in non-polar solvating solvent. The different approaches, which are used to this type of mixtures, are briefly reviewed. Theoretical expressions are given for the analysis of thermodynamic functions (activity coefficients of components, excess Gibbs energy, enthalpy of mixing), static dielectric constant, dipole correlation factor in the framework of the unified quasichemical approach. The structural-stoichiometric model is considered which implies formation of chain alcohol aggregates of arbitrary length forming complexes with dioxane molecules, and cyclic tetramers of alcohol. The non-ideal mixture of aggregates was described in the framework of the QuasiChemical Nonideal Solution (QCNAS) model [1-3]. QCNAS model takes into account both the universal (dispersion, dipolar, and attractive) and specific intermolecular interactions like H-bonds in the mixture of aggregates. Describing processes of aggregation is given in terms of activities of aggregates and thus the equilibrium constants obtained are transferable from one mixture to other one. The general scheme for describing thermodynamic and dielectric properties of mixtures of polar associating solute in non-polar solvating solvent in the whole composition range is developed. The relationships of excess thermodynamic functions and permittivity with thermodynamic parameters of aggregation and structure of supramolecular species are given. The influence of non-rigidity of 1,4-dioxane molecules leading to polar conformers of that on the permittivity is discussed. The cooperative character of aggregation was described on the thermodynamic level due to difference between equilibrium constants for formation of dimers and higher aggregates. The thermodynamic parameters of chain-like and cyclic aggregation (constants of equilibrium, enthalpy, and entropy) as well as the structural parameters of aggregates have been obtained. The integral (average number of aggregation) and differential (distribution functions of aggregates on size and weight and molecules involved in H-bonding on numbers on bonds) parameters of aggregation were calculated. The concentration dependencies of those are discussed. The comparative role of chain-like and cyclic aggregates of alcohol on the properties of mixtures is revealed. The large supramolecular aggregates, which involve tens of molecules in the mixtures rich by alcohol, have been found. The comparison of the data obtained with those from spectroscopic, diffraction and simulation techniques are given. It was shown that the model proposed allows giving the unified description of mixing functions, dielectric constant and carrying out the quantitative analysis of association equilibria and intermolecular interactions in the mixture dioxane-alcohol in the whole composition of mixture range and in the wide temperature interval.

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[1] V.A. Durov, "Models in Theory of Molecular Liquid Mixtures: Structure, Dynamics, and Physicochemical Properties", In: Novel Approaches to the Structure and Dynamics of Liquids: Experiments, Theories, and Simulations; / J. Samios, V.A. Durov, Eds./ NATO Science Series. II. Mathematics, Physics and Chemistry. V.133. Dordrecht, Kluwer, 2004, p. 17-40.
[2] V.A. Durov, *Pure and Appl. Chem*. **76**, 1 (2004).
[3] V.A. Durov, *J. Mol. Liquids* **118**, 101 (2005).