Models of Aggregation Phenomena in Liquid Mixtures: Thermodynamic and Related Properties

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The approaches to describing aggregation phenomena in liquid mixtures are reviewed. The main attention are given to extended quasichemical models applying for describing equilibrium and non-equilibrium processes, occurring in liquids during molecular thermal motion (aggregation, energy transfer, intramolecular transitions, and related fluctuation phenomena). The concept of internal variables of different nature and tensor dimension which allows including in unified consideration both equilibrium and non-equilibrium properties of a matter is discussed. These models are formulated in the framework of the non-ideal liquid mixtures for those Quasichemical Nonideal Associated Solutions (QCNAS) model [1-3] is developed. QCNAS model takes into account both the universal (dispersion, dipolar, and attractive) and specific intermolecular interactions like H-bonds. The models of aggregates include in unified consideration composition and structure polyvariability of supramolecular forms. 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 relationships between thermodynamic properties of mixtures (Gibbs energy, enthalpy, entropy, and corresponding excess thermodynamic functions of mixtures) and molecular interactions, and supramolecular structure of liquid systems were established. The models for describing permittivity and optical properties related with fluctuation phenomena and Rayleigh light scattering are discussed. The relationships permittivity with thermodynamic of aggregation and structure of aggregates are given. The fluctuation's theory are reviewed with emphasis to developing models for describing supramolecular ordering in non-ideal liquid systems and revealing the role of fluctuations for macroscopic properties of liquids. The procedure for constructing fluctuation parts of the thermodynamic potentials (Helmgoltz and Gibbs energy for the closed systems, and the grand thermodynamic potential for the opened systems) starting from microscopic statistical ensembles is developed. These thermodynamic potentials describe the non-equilibrium both isotropic and anisotropic states of a matter, which are characterized by the internal parameters of different tensor dimension. The contributions from fluctuations of internal parameters to thermodynamic properties (heat capacity, compressibility, thermal expansion coefficient, etc.) as well as the relationships of those with relaxation characteristics are discussed [4]. The extension of the Lorenz internal field approach for anisotropic fluctuation states of matter is given and thus the extended Lorenz-Lorentz electrooptical equation of state was derived. The applications to isotropic and anisotropic light scattering are discussed [5]. The application of the approach developed to study structural and thermodynamic parameters of aggregation due to noncovalent intermolecular interactions like H-bonds from analysis a set of thermodynamic, dielectric, diffraction, light scattering, and spectroscopic techniques are given. Special attention is given to investigating structural features of aggregation and results obtained are compared with data extracted from diffraction, spectroscopic and computer simulation techniques. The long-ranged molecular correlations in liquids due to H-bonding at the ambient parameters of state were revealed. The macroscopic manifestations of supramolecular ordering of liquids on properties of those are discussed.

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