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Supramolecular structure and physicochemical properties of the trichloromethane–ethanol mixtures

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Abstract

The excess thermodynamic functions (Gibbs energy, enthalpy, and entropy) and the dielectric permittivity of the trichloromethane–ethanol solutions have been analyzed in the entire range of compositions and in a wide temperature range in the framework of the quasichemical model of nonideal associated solution (QCNAS). The model of supramolecular structure, taking into account the chain-like and cyclic association of alcohol molecules and complexation of alcohol aggregates with trichloromethane, is able to reproduce the physicochemical properties of the mixtures with good accuracy. The equilibrium constants, enthalpies and entropies of aggregation, and structural parameters of supramolecular aggregates have been determined. Distribution functions of aggregates over size and structure have been calculated. Supramolecular ethanol aggregates with long-range molecular correlations, which extend beyond the nearest coordination shells have been revealed. Specific interactions are shown to give the main contribution to the positive deviations from the ideal solution behavior. Positive deviation of the dipole correlation factor from unity is due to predominantly parallel orientation of the dipoles in the ethanol aggregates and in the complexes with trichloromethane. The influence of ethanol association (linear and cyclic) as well as solvation on the physicochemical properties of the mixtures is discussed.

Keywords: Liquid mixture; Thermodynamics; Supramolecular liquid structure; Hydrogen bond; Long-range correlations

1. Introduction

1.1. Quasichemical models

In the recent years, quasichemical models [1–8] have been extensively used to study the supramolecular structure and physicochemical properties of a number of nonelectrolyte mixtures [9–15]. These models not only provide a unified approach for correlating various macroscopic properties (thermodynamic, dielectric, optic, and kinetic) on the molecular basis, but also allow studying the supramolecular ordering of H-bonded molecular liquids, including the long-range molecular correlations, which extend beyond the nearest coordination shells. The review [8] contains the most updated collection of the thermodynamic parameters of the aggregation equilibria studied earlier.

In the quasichemical models, the processes are represented by the equations of chemical reaction:

$$\sum_i \nu_{i\alpha} M_i \underset{k'_\alpha}{\overset{k_\alpha}{\Leftrightarrow}} \sum_i \nu'_{i\alpha} M_i, \quad \alpha = 1, 2, \ldots, r, \tag{1}$$

$$\mathrm{d}\xi_\alpha = \frac{\mathrm{d}n_{i\alpha}}{\Delta\nu_{i\alpha}},\ \Delta\nu_{i\alpha} = \nu'_{i\alpha} - \nu_{i\alpha},\ A_\alpha = -\sum_i \mu_i \Delta\nu_{i\alpha}, \tag{2}$$

where M_i designates the i-th reagent, $\upsilon_{i\alpha}, \upsilon'_{i\alpha}$ are its stoichiometric coefficients in the reaction α. These processes are characterized by the extent (degree of advancement) ξ_α and the affinity A_α, μ_i is the chemical potential of the i-th reagent, $n_{i\alpha}$ is the number of moles of the i-th reagent, k_α and k'_α are the rate constants for direct and reverse processes, respectively. For the nonequilibrium states, the extents ξ_α are independent parameters and the corresponding affinities A_α are not equal to zero.

The extents $\{\xi_\alpha\}$ represent scalar internal variables. Internal vector variables represent, for instance, fluctuating local velocities or polarization. Tensor variables are applied in order to describe anisotropic states of system, examples of mechanical

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ones being the tensors of deformation $\{u_{ik}\}$ and stress $\{\sigma_{ik}\}$. Internal tensor variables $\{\eta_{\beta,ik}\}$ characterize nonequilibrium anisotropic states of matter (e.g. the local polarizability tensor) and they are not generally reduced to mechanic ones. The concept of internal variables is especially important for the theory of irreversible processes [4–8,16].

Quasichemical models combine both macroscopic and molecular theories. They can be considered as an extension of chemical thermodynamics and kinetics to the treatment of processes in matter, e.g. spatial reorganizations of supramolecular structures as well as energy transfer between molecular degrees of freedom, conformational transitions of molecules, and related fluctuation phenomena. Molecular models are used both to specify the nature of the process and to derive equations for physicochemical properties.

The term “quasichemical models” [1–8] underlines the fact of using the chemical language to describe the wide spectrum of the processes occurring in matter, which in general are not followed by the change of the chemical nature of reagents, and thus allows considering different properties within the unified approach. These models are named sometimes as association or chemical ones [17], though their applicability is much wider [1–8]. These models should not be missed with the “quasichemical approach” introduced by Guggenheim [18] for estimation of the partition function in the lattice model proposed for thermodynamic functions of the mixtures. The latter has only a formal analogy with the real processes occurring in matter during molecular thermal motion [1–8].

The models of supramolecular aggregates polyvariable in structure and composition have been constructed. The models developed take into account the cooperative (collective) character of H-bonding. Commonly, this means the dependence of the H-bonding energy on the size of the aggregates. This simplest type of H-bond cooperativity was accounted for on the thermodynamic level using different equilibrium constants for dimerisation and the formation of higher aggregates. More complicated types of cooperativity have been studied. Matrix methods were developed to describe both microscopic properties of aggregates and the macroscopic properties of mixtures.

The polyvariability of aggregates in structure and composition gives the possibility to study the systems self-organized by noncovalent directed interactions like H-bonds, keeping the information in binary or more multivalent forms. Thus, controlling both the compositional and structural reorganization of supramolecular aggregates enables molecular information processing, especially in the living nature. The description of the cooperative (collective) character of the aggregation gives the basis for “molecular understanding” of the complementary phenomena in biological systems [1–8].

1.2. Trichloromethane–ethanol mixtures

The present work is an application of the quasichemical approach to the trichloromethane–ethanol mixtures, a system with a complex supramolecular structure. The components of these mixtures are important compounds at both practical and theoretical levels [19]. We shall focus here on the thermodynamic (activity coefficients γ_A, γ_B, excess Gibbs energy G^E, enthalpy H^E, and entropy S^E) and dielectric (permittivity ε_s) properties of the mixtures.

The vapor–liquid equilibrium, which is used in this work as a source of experimental activity coefficients γ_A, γ_B and excess Gibbs energy G^E, was studied in the chloroform–ethanol system in the temperature range 308–328 K [20–22]. The ethalpies of mixing H^E of solutions were studied in the temperature range 298–323 K [23,24]. The excess Gibbs energy of solutions is positive and passes through a maximum as the temperature is raised. The composition dependence of the excess enthalpy H^E and entropy S^E of the solutions is S-shaped. The thermodynamic functions are positive at low percentage of alcohol and negative at the ethanol end.

The static permittivity ε_s of the chloroform–ethanol mixtures measured at 298 K [25] shows negative deviations from additivity. The thermodynamic and dielectric properties of the chloroform–ethanol system are in general similar to those of the chloroform–methanol system [15] and a similar supramolecular structure, based on the alcohol linear and cyclic aggregation and complex formation with trichloromethane, is expected in this system. The aggregation occurs due to the hydrogen bonds between ethanol molecules (H–O $\cdots$ H–O), while complex formation is due to the hydrogen bonds between ethanol and trichloromethane molecules (H–O $\cdots$ H–C).

The role of the alcohol–alcohol hydrogen bonds have been examined and discussed in detail earlier [1–8]. According to various data, the enthalpy of formation of the hydrogen bond H–O $\cdots$ H–O lies in the interval from -15 to -25 kJ/mol. The hydrogen bond H–O $\cdots$ H–C between ethanol and trichloromethane molecules has been detected by IR spectroscopy [26].

The thermodynamic functions of the trichloromethane–ethanol mixtures were correlated using various models in [27–31]. In [27–29], both the excess Gibbs energy G^E and the enthalpy of mixing H^E of the solutions were reproduced; the model took into account the chain-like and cyclic association of the alcohol and the formation of complexes between the ethanol aggregates and trichloromethane molecules. The contribution from nonspecific interactions was calculated using empirical equations: Wilson [27], UNIQUAC [28], and NRTL [29]. The enthalpies of association of alcohol and complexation with trichloromethane were estimated as $\Delta H = -25$ kJ/mol and $\Delta H_s = -24.5$ kJ/mol, respectively. The excess functions G^E and H^E of the trichloromethane–ethanol mixtures were correlated also in the framework of the lattice Barker’s model [31]. An attempt was made to describe the thermodynamic properties of the system using the lattice-fluid model, although only qualitative agreement with experiment was achieved [30].

Thus, in the works [27–31] the thermodynamic functions of solutions were correlated using a large set of adjustable parameters, which were not tested against spectral, dielectric, and other properties (for details, see [1–8]). The model of association was chosen largely arbitrary; moreover, the methods for describing association equilibria were combined with the