

Modeling of Supramolecular Ordering and Physicochemical Properties in Cyclohexane–Ethanol Mixtures

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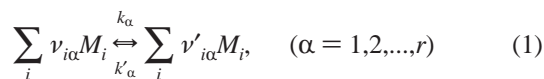
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The quasichemical model of the nonideal associated solution (QCNAS) was used to analyze the excess thermodynamic functions and permittivity of cyclohexane–ethanol mixtures in the entire range of compositions and in a wide temperature range. A new model of supramolecular organization was substantiated, taking into account chain and cyclic aggregation of alcohol with the formation of chain aggregates of arbitrary size, which describes a set of physicochemical properties of this mixture with complicated behavior of both thermodynamic and dielectric properties. Equilibrium constants and thermodynamic parameters of H bonding having cooperative character and integral and differential characteristics of aggregation and the structural parameters of aggregates were determined. It was established that the role of nonpolar cyclic structures increases as alcohol concentration decreases. The model describes the permittivity of solutions in the entire range of compositions and reproduces a minimum of the dipolar correlation factor in the range of dilute alcohol solutions. The new data obtained on the supramolecular ordering characterized by the long-range molecular correlations due to H bonding are discussed in detail.

Introduction

Quasichemical models, which can be used to analyze the supramolecular structure and physicochemical properties of solutions in terms of a unified approach, were extensively applied to study supramolecular ordering and properties of pure liquids and mixtures.^{1–6} In the quasichemical models, the processes are represented by the equations of chemical reaction:



$$d\xi_\alpha = \frac{dn_{i\alpha}}{\Delta\nu_{i\alpha}}, \quad \Delta\nu_{i\alpha} = \nu'_{i\alpha} - \nu_{i\alpha}, \quad A_\alpha = -\sum_i \mu_i \Delta\nu_{i\alpha} \quad (2)$$

where M_i designates the i th reagent, and $\nu_{i\alpha}$ and $\nu'_{i\alpha}$ are its stoichiometric coefficients in the reaction α . These processes are characterized by the extent (or degree of advancement) ξ_α and the affinity A_α (eq 2), where μ_i is the chemical potential of the i th reagent, and rate constants for direct k_α and reverse k'_α processes. For nonequilibrium states, the extents ξ_α are independent parameters, and the corresponding affinities A_α are not equal to zero.

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”^{1–6} underlines the fact of using 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, though their applicability is much wider.^{1–6} These models should not be missed with the “quasichemical approach” introduced by Guggenheim⁷ 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.^{1–6}

Quasichemical models of association processes have been applied in several instances to thermodynamic and spectroscopic properties of liquid systems.^{1–6,8–11} Recently, along with the elaboration of the aggregation models and the thermodynamics of the liquid systems self-organized due to noncovalent molecular interactions, this approach has been extended to dielectric, optic, and kinetic properties of mixtures. Among the properties considered, which are defined by different molecular parameters, are thermodynamic functions, the Gibbs energy G , the enthalpy H , the entropy S , and the corresponding excess functions for mixtures, G^E , H^E , and S^E , the activity coefficients of the components γ_A and γ_B , the dielectric permittivity ϵ_S , and optical properties such as Rayleigh ratios for isotropic and anisotropic light scattering, R_{is} and R_{an} .^{1–6}

In comparison with the previous attempts for considering association phenomena in mixtures, which are reviewed in refs 1–6, the quasichemical model of nonideal solution (QCNAS) first gives quite detailed description of the nonideality of the aggregate mixtures due to dipolar, dispersion, and specific molecular interactions;^{11–13} second, this model includes detailed description of structure, composition, electric, and optic properties of the aggregates; and third, this approach combines unified description, not only of thermodynamic functions of mixing,

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but also permittivity and optic properties of mixtures. These properties are defined by different molecular parameters, and therefore, it allows obtaining detailed data both on the structure of supramolecular aggregates and thermodynamics of their formation. Especially, the new possibilities should be underlined for revealing and studying the long-range molecular correlations, which are impossible to investigate by other techniques.^{1–6}

At the initial construction of the approach developed a mixture of associated species with arbitrary compositions, and different ways of H bonding between the molecules in the aggregates was introduced. These aggregates possess polyvariability both in composition and structure because any molecule in the mixture may be located on any site of an aggregate. Different ways of bonding lead to the structural multivariance of the aggregates: starting from the “root” molecule, various ways for aggregate growth are possible. Thus, both the structural and the compositional multiformity of aggregates lead to new types of their structures. For instance, even for chainlike aggregates of homogeneous composition, new types of the supramolecular structures were established.^{1–6}

The model developed takes 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 by introducing different equilibrium constants for dimerization and the formation of higher aggregates. More complicated types of cooperativity have been studied. Matrix methods were developed both for microscopic properties of aggregates and the macroscopic properties of mixtures.^{1–6} It should be underlined also that the approach developed includes the unique consideration of a wide spectrum of aggregation processes with species are different both in composition and structure. In particular, it allows taking into consideration the chemical nature of solvent (inert, nonpolar or polar, solvating, associating etc.).^{1–6} In this regard, it should be noticed that common analysis^{8–10} of aggregation processes is based on the simplest model of associating substance in inert solvent.

This work is concerned with the binary cyclohexane–ethanol solutions. This mixture consists of the polar aggregating substance in the nonpolar “inert” solvent and is characterized by the large positive values of the excess Gibbs energy G^E and enthalpy H^E . The investigation of this mixture allows us to study the structure of alcohol aggregates not complicated by specific interactions of alcohol with solvent, as in the case of solutions of alcohol in nonpolar solvating solvents, e.g., 1,4-dioxane,^{14,15} tetrachloromethane,^{16,17} and polar solvating solvent, e.g., propanone.¹⁸

The cyclohexane–ethanol mixtures were investigated earlier by thermodynamic and dielectrometric methods^{19–22} (the vast collection of thermodynamic data is presented in ref 22) as well as by IR and NMR spectroscopy.^{23,24} In our theoretical analysis, we used the data obtained in the whole range of solution compositions and in the widest available temperature range. The thermodynamic data used were tested for thermodynamic consistency by Herington–Redlich–Kister criteria.²⁵

The vapor–liquid equilibrium in the cyclohexane–ethanol mixtures was studied at 273–338 K (see ref 22), and the heats of mixing H^E were measured at 280–318 K.^{20,22} The excess Gibbs energy G^E and enthalpy H^E are positive, which qualitatively corresponds to the prevailing role of H bond breakage at the forming of mixture from components. At the same time, the excess entropy of solution S^E is negative at all solution compositions, which proves the existence of more ordered

structures in cyclohexane–ethanol solutions in comparison with a hypothetical ideal reference solution.²⁵ In fact, the negative value of S^E is not direct evidence for association, as it was shown in ref 26, but it will be revealed that the contribution of aggregation in the studied systems is quite important and results in negative S^E values.

The permittivity ϵ_s of cyclohexane–ethanol solutions was measured at 268–323 K (see, for example, ref 21). It shows negative deviations from additivity $\Delta\epsilon_s = \epsilon_s - (\epsilon_{sA}^0\varphi_A^0 + \epsilon_{sB}^0\varphi_B^0) < 0$, where A denotes cyclohexane, B denotes ethanol, and φ_A^0 and φ_B^0 are the volume fractions of the components.

The concentration dependence of the Kirkwood correlation factor of solution g_s^d , calculated from experimental data (eq 21) is more complex: g_s^d is larger than unity in the area of high alcohol concentration. But in dilute alcohol solutions ($x_B^0 \leq 0.2$ mole fraction), the correlation factor passes through a minimum, $g_s^d < 1$, that specifies qualitatively an essential role of low-polar alcohol aggregates in this concentration range. This dependence of correlation factor g_s^d on mixture composition is fully different from that observed for the mixtures such as 1,4-dioxane–alcohol¹⁴ and tetrachloromethane–methanol,¹⁵ and therefore should be investigated in detail.

Fourier transform infrared (FTIR) spectroscopic investigations of dilute cyclohexane–ethanol solutions were carried out at 283, 298, and 313 K.²⁴ The authors specified that the limits of applicability of analysis given is $x_B^0 \leq 0.2$ mole fraction. Despite that, the experimental data were presented in the concentration range $x_B^0 \leq 0.05$ mole fraction.

The model of alcohol aggregation presented in ref 24 includes formation of dimers and pentamers with the corresponding equilibrium constants of aggregation K_2 and K_5 . But one should note that, despite of excellent quality of experimental data, the model $A_1 + B_1 + B_2 + B_5$ applied for the cyclohexane–ethanol solution in ref 24 and, consequently, the thermodynamic data of aggregation obtained in ref 24, does not seem to be proved enough. In the paper,²⁴ the $\sim 3630\text{ cm}^{-1}$ adsorption band was assigned solely to alcohol monomers, and thus the influence of terminal OH groups of chain alcohol aggregates was not taken into account (see, e.g., refs 2, 3, and 27–30). The formal procedure for resolution of monomer, dimer, and polymer (pentamer) bands is not unequivocal enough due to strong band overlapping. Effects of an internal field³¹ and, therefore, possible concentration dependence of absorption coefficients of alcohol monomers and aggregates were not considered. The authors²⁴ postulated only chain aggregates, but such a model poorly describes the dielectric properties of the dilute cyclohexane–ethanol solutions, as it was mentioned above, because dipole correlation factor $g_s^d < 1$ in this composition range and, thus, the evidence of the important role of the nonpolar cyclic aggregates, is clear. Third, to describe thermodynamic properties of mixtures, the authors²⁴ applied the UNIQUAC model,^{32,33} expanded by association processes by using a number of additional assumptions. However, no calculations of thermodynamic properties of solutions confirming validity of the model used in a wide concentration range were carried out.

As a result, the average number of aggregation of pure ethanol \bar{n}_B we calculated by using the data presented in ref 24 ($\bar{n}_B \approx 4.7$, $T = 298\text{ K}$) seems underestimated compared to the results of diffraction,^{34,35} spectroscopic,²⁷ thermodynamic, and dielectrometric^{1–6} methods. The model²⁴ also does not meet the results of computer simulation,^{36–39} which proves the predominant role of the continuous chainlike aggregation in pure alcohols. It is necessary to note that, in computer modeling, the data concerning long-range correlations of molecules can be artificially

disregarded due to the periodic boundary conditions or limited time of calculations.^{1–6} So, the average number of aggregation obtained by computer simulation methods using small number of particles in the basic cell^{36,37} is essentially underestimated as well.^{1–4,16,38}

The analysis of activity coefficients, permittivity, and spectroscopic data of cyclohexane–ethanol solutions using the aggregation model that takes into account chain and cyclic alcohol aggregates is carried out in ref 30. The authors³⁰ utilized the basic model of the ideal associated solution (IAS).⁹ The contribution from nonspecific interactions was treated as an additive term calculated by the Hildebrand model of regular solution. However, the IAS model, especially being applied to strongly aggregated mixtures, has principal drawbacks, most important from them is ignoring the role of difference of aggregates in size and also the simple addition of the physical contribution to the function of mixing used in ref 30 is not thermodynamically consistent.^{1–6,40}

Thus, the purpose of the present work was to analyze a set of thermodynamic and dielectric properties of cyclohexane–ethanol mixture within the framework of a unified quasichemical approach and to study both the structural and thermodynamic characteristics of supramolecular organization of these systems.

Theoretical

The model used for cyclohexane–ethanol mixtures takes into account formation of the chainlike aggregates with an arbitrary number of alcohol molecules and cyclic nonpolar alcohol aggregates, consisting of four molecules: $A_1 + B_1 + B_2 + B_3 + \dots + B_n + \dots + B_{4,\text{cycl}}$.

The backgrounds for chainlike aggregation of alcohols are reviewed in refs 1–6. The cyclic tetramers of alcohol are the most probable among its cyclic aggregates according to the computer simulation data on alcohols and their solutions.^{36–39} It was shown that the role of cyclic aggregates of alcohol is most important in the composition of a mixture poor in alcohol. Aggregation of alcohol molecules due to H bonding $\text{H}-\text{O}\cdots\text{H}-\text{O}$ is described by three equilibrium constants: K for dimerization, K' for the formation of higher aggregates starting from trimers, and $K_{4,\text{cycl}}$ for formation of cyclic tetramers. The solvation of molecules and aggregates of ethanol by cyclohexane was not taken into account because cyclohexane was treated as an inert solvent.

The aggregates mixture has been described in the framework of the quasichemical model of nonideal associated solution (QCNAS).^{1–6,41} This model takes into account the nonideality of the aggregates mixture due to short-range repulsive and attractive like H bonds intermolecular forces and the physical nonspecific molecular interactions subdivided to the dispersive and dipolar ones. Thus, the activity coefficients of the aggregates include three in general interrelated contributions: $\gamma_i = \gamma_i^{\text{ass}} \cdot \gamma_i^{\text{dis}} \cdot \gamma_i^{\text{dip}}$. The first of them has been described in the framework of Flory's statistics, the second one in continuous approach, and the last one on the basis of the modified Onsager's reaction field concept taking into account the structure of the species.

It should be underlined that the approach used has been started from the consideration of the partition function of the aggregate's mixture and followed by constructing expressions for the chemical potentials of the aggregates. Thus, this approach possesses by thermodynamic consistency in contradiction with usually applied additive combination of the aggregation and physical contributions to the thermodynamic functions (e.g., compare with ref 30).

The equilibrium constants of the aggregation process are defined by thermodynamic equations in terms of the activities of associated species:

$$K^T = \frac{a_{B_2}}{a_b^2}, \quad K^{T'} = \frac{a_{B_{n+1}}}{a_{B_n} a_b}, \quad n \geq 2, \quad K_s^T = \frac{a_{AB}}{a_a a_b},$$

$$K_s^{T'} = \frac{a_{AB_{n+1}}}{a_b a_{AB_n}}, \quad n \geq 2, \quad K_{4,\text{cycl}}^T = \frac{a_{B_4}}{a_b^4} \quad (3)$$

where a_a and a_b denote the activities of monomer molecules A and B, a_{B_n} , a_{AB_n} are activities of aggregates and complexes. The relationships of the thermodynamic equilibrium constants expressed by the activities of the aggregates $\{a_i\}$, K^T , $K^{T'}$, $K_{4,\text{cycl}}^T$ (eq 3), and the corresponding concentration “equilibrium constants” expressed by the molar concentrations $\{c_i\}$, K , K' , $K_{4,\text{cycl}}$, are given by the equations of the quasichemical model of nonideal associated solution (QCNAS).^{1–6,41} These equations have a form $K^T = K \cdot \Gamma^{\text{dis}} \cdot \Gamma^{\text{dip}}$, where the terms Γ^{dis} and Γ^{dip} are given by the expressions for the contributions of the “physical” dispersion and dipolar forces to the activity coefficients of the aggregates $\{\gamma_i^{\text{dis}}\}$, $\{\gamma_i^{\text{dip}}\}$, and their form is formally analogous to equilibrium constants with replacement of activities to the corresponding activity coefficients. The values Γ^{dip} and Γ^{dis} are estimated in the framework of the QCNAS model. The concentration “equilibrium constants” K include nonideality of the aggregates mixture due to the difference in their “sizes”, characterizing the repulsive part of the intermolecular potential, which are described by the respective activity coefficients $\{\gamma_i^{\text{ass}}\}$ at the formal transforming from the molar fractions of the aggregates $\{x_i\}$ to their molar (volume) concentrations $\{c_i\}$ ($\{\varphi_i\}$).^{1–6} In general, these equations allow us to express the dependence of the concentration “equilibrium constants” K , applied for the estimation of the aggregate concentrations on the mixture composition. The set of equilibrium constants $\{K^T\}$ is enough for describing processes of aggregation in the mixture in the framework of the selected scheme of aggregation.

It was substantiated that the states of $\text{H}-\text{O}\cdots\text{H}-\text{O}$ bonds differing in the orientation of alcohol molecules in aggregates are the same in a given aggregate, i.e., they refer to one of the two types of bonds described in detail in refs 1–6 and 42. This corresponds to the model of aggregates with correlated collective states of the H bonds in the aggregates.^{1–6,42} The mutual orientations of the alcohol molecules in aggregates are described by the matrixes of transition between the coordinate systems of neighboring molecule $\langle \mathbf{T}_{bb}^{(1)} \rangle$, $\langle \mathbf{T}_{bb}^{(2)} \rangle$, where the superscripts (1) and (2) correspond to two different modes of formation of hydrogen bonds, whereas the angle brackets denote averaging over the angle of rotation φ of the molecules in aggregates. The elements of the matrixes $\langle \mathbf{T}_{bb}^{(1,2)} \rangle$ ⁴²

$$\langle \mathbf{T}_{bb}^{(1,2)} \rangle = \begin{pmatrix} 0.346 - 0.259\eta_{1,2} \mp 0.551\beta_{1,2} & -0.334 - 0.268\eta_{1,2} \mp 0.571\beta_{1,2} & \pm 0.793\eta_{1,2} - 0.373\beta_{1,2} \\ 0.021 - 0.624\eta_{1,2} \pm 0.306\beta_{1,2} & -0.020 - 0.646\eta_{1,2} \pm 0.316\beta_{1,2} & 0.440\eta_{1,2} - 0.898\beta_{1,2} \\ \pm 0.630 \pm 0.163\eta_{1,2} + 0.292\beta_{1,2} & \mp 0.609 \pm 0.169\eta_{1,2} + 0.302\beta_{1,2} & -0.421\eta_{1,2} \pm 0.235\beta_{1,2} \end{pmatrix} \quad (4)$$

are determined by the geometric structure of the molecules and aggregates and depend on the orientational parameters $\eta = \langle \cos \varphi \rangle$, $\beta = \langle \sin \varphi \rangle$, which characterize the width and the asymmetry of the potential of rotation $U(\varphi)$ around H bonds in aggregates.^{42,43} In general, matrixes $\langle \mathbf{T}_{bb}^{(1,2)} \rangle$ give a quite detailed description of the molecular structure of the aggregates, including internal degrees of freedom.

The activity coefficients of the components γ_A , γ_B and excess Gibbs energy G^E , enthalpy H^E , and entropy S^E of the mixture calculated within the framework of model QCNAS^{1–6,41} are given by expressions:

$$\gamma_{A(B)} = \gamma_{A(B)}^{\text{ass}} \gamma_{A(B)}^{\text{dip}} \gamma_{A(B)}^{\text{dis}}, \quad H^E = H^{E,\text{ass}} + H^{E,\text{dip}} + H^{E,\text{dis}} \quad (5)$$

where individual, in general interrelated, terms reflect the contributions to the thermodynamic nonideality of the solution from the aggregation (ass), dispersion (dis), and dipole (dip) molecular interactions. The starting point at the derivation of eq 5 was the Prigogine–Defay equations⁹ $\mu_A = \mu_a$, $\mu_B = \mu_b$, relating the chemical potentials of solution components μ_A and μ_B and those of monomer molecules μ_a and μ_b . The upper case letters A and B refer to solution components, and the lower case ones *a* and *b* refer to monomer molecules. The symmetric reference system^{9,25} for the activities of components is used in eq 5. The expressions for the chemical potentials of the monomers μ_a and μ_b were derived in the framework of the QCNAS model characterized above.^{1–6,41}

The contributions from the association interaction to the activity coefficients of the components, which take into account hydrogen bonding and repulsion interactions γ_A^{ass} and γ_B^{ass} , are:

$$\gamma_A^{\text{ass}} = \frac{c_a V_{m,A}}{x_A^0} \exp\left(1 - \frac{V_{m,A}}{n_{AB} V_m}\right), \quad \gamma_B^{\text{ass}} = \frac{c_b}{x_B^0 \bar{c}_b} \exp\left(\frac{1}{\bar{n}_B} - \frac{V_{m,B}}{n_{AB} V_m}\right) \quad (6)$$

In eq 6, \bar{c}_b is the molar concentration of monomers B in pure component B; V_m , $V_{m,A}$, and $V_{m,B}$ are the molar volumes for the solution and the components A (cyclohexane) and B (ethanol), respectively; $x_{A,B}^0$ are the mole fractions of the components; n_{AB} is the average number of aggregation in the solution; \bar{n}_B is the average number of aggregation in pure component B.

The multipliers $\gamma_{A,B}^{\text{dis}}$ in eq 5 describe the contribution of dispersion interactions to the nonideality of a solution:

$$RT \ln \gamma_A^{\text{dis}} = \beta_{AB} V_{m,A} (\varphi_B^0)^2, \quad RT \ln \gamma_B^{\text{dis}} = \beta_{AB} V_{m,B} (\varphi_A^0)^2 \quad (7)$$

The parameter β_{AB} is given as follows:

$$\beta_{AB} = \frac{N_o}{2} \left(\frac{C_{aa} \Phi_A^2}{V_{m,A}} + \frac{C_{bb} \Phi_B^2}{V_{m,B}} - \frac{2C_{ab} \Phi_A \Phi_B}{(V_{m,A} V_{m,B})^{1/2}} \right) \quad (8)$$

where N_o is the Avogadro number, $V_{m,A}$ and $V_{m,B}$ are the molar volumes of the components, C_{ij} are the coefficients for the dispersion potential $U_{ij} = -C_{ij}\alpha_i\alpha_j/R^6$, and α_i is the polarizability of the *i*th component. The quantities Φ_i and C_{ij} (e.g., if the dispersion force potential is written by the classic London equation) are

$$\Phi_i = \frac{\epsilon_{\infty,i} - 1}{\epsilon_{\infty,i} + 2}, \quad C_{ij} = \frac{3}{2} \frac{I_i I_j}{I_i + I_j}, \quad i, j = A, B \quad (9)$$

where I_i is the ionization potential, $\epsilon_{\infty,i}$ (*i* = A, B) is deformation permittivity of *i*th component, which is defined by both electronic and nuclear contributions.^{41,44}

The multipliers $\gamma_{A,B}^{\text{dip}}$ in eq 5 describe the contribution from dipole interactions to the nonideality of a solution:^{1–6,41,44}

$$RT \ln \gamma_A^{\text{dip}} = -\frac{\mu_a^2}{V_{m,A}} (f - \bar{f}_A) + x_B^0 S, \quad RT \ln \gamma_B^{\text{dip}} = -\frac{\mu_b^2}{V_{m,B}} (f - \bar{f}_B) + x_A^0 S \quad (10)$$

where μ_a and μ_b are the dipole moments of molecule *a* and *b*, and expressions both for *f* in terms of the static ϵ_s and deformation ϵ_∞ permittivity of a solution, and the value *S*, related to the dipole moments of monomers μ_i and aggregates $M_{A_p B_q}$ ² are in refs 41 and 44:

$$f = \frac{4\pi N_o^2 (\epsilon_s - 1)(\epsilon_\infty + 2)}{9 (2\epsilon_s + \epsilon_\infty)} \quad (11)$$

$$S = -\frac{4\pi N_o^2 V_m}{9} \left(\frac{\partial \epsilon_s}{\partial x_A^0} \right) \frac{(\epsilon_\infty + 2)^2}{(2\epsilon_s + \epsilon_\infty)^2} \sum_{p,q} c_{A_p B_q} \frac{\langle M_{A_p B_q}^2 \rangle}{V_{m,A_p B_q}} \quad (12)$$

The values \bar{f}_A and \bar{f}_B in eq 10 are values of function *f* (eq 11) for pure components A and B. Therefore, eqs 10–12 express dipolar contribution to activity coefficients of the mixture components, which take into account via concentration and dipole moments of aggregates the supramolecular structure of the mixture.

The approach developed relates the thermodynamic nonideality of the mixtures to molecular properties, rather than employing empirical parameters, and allows going beyond the approach of just short-range interactions. As it was mentioned, the thermodynamic nonideality of an associated species mixture leads to the dependence of the “equilibrium constants”, expressed by the molar concentrations from the solution composition, and this is highly important for correct study of the aggregation.^{1–6}

The average numbers of aggregation of the mixture, n_{AB} , and component B, n_B , represent the integral characteristics of the association. For the model presented, they are given by the equations

$$n_{AB} = \frac{c_A^0 + c_B^0}{c_a + c_{\text{sum},B}}, \quad n_B = \frac{c_B^0}{c_{\text{sum},B}} \quad (13)$$

$$c_{\text{sum},B} = c_b + \sum_{n=2}^{\infty} \sum_{l=1}^2 c_{B_{n,l}} + c_{B_{4,\text{cycl}}} = c_b + \sum_{n=2}^{\infty} c_{B_n} + c_{B_{4,\text{cycl}}} = c_b + \frac{2Kc_b^2}{1 - K'c_b} + K_{4,\text{cycl}} c_b^4 \quad (14)$$

$$c_{B_n} = 2c_{B_{n,1(2)}} = 2Kc_b^2 (K'c_b)^{n-2}, \quad c_B^0 = c_b \left(1 + \frac{2Kc_b(2 - K'c_b)}{(1 - K'c_b)^2} \right) + 4K_{4,\text{cycl}} c_b^4 \quad (15)$$

where c_B^0 is the molar concentration of ethanol, $c_{B_{n,l}}$, (*n* ≥ 2, *l* = 1, 2), $c_{B_{4,\text{cycl}}}$, denote the concentration of the aggregates, index *l* (*l* = 1, 2) means the states of the H bonds in the aggregates, $c_{\text{sum},B}$ is the total concentration of monomers and aggregates of the alcohol. Equation 15 has been applied for calculations of the molar concentrations of the monomers c_b . In eqs 14–15, it has been taken into account that there are two

states of the alcohol aggregates B_n , AB_n ($n \geq 2$), consisting of n alcohol molecules with the equal states of the H bonds, and those are the enantiomers at the respective angles of the rotation in the aggregates φ .^{41,42} The total molar concentrations of the aggregates B_n , AB_n are denoted as:

$$c_{B_n} = 2c_{B_{n,1}} = 2c_{B_{n,2}}, \quad c_{AB_n} = 2c_{AB_{n,1}} = 2c_{AB_{n,2}}, \quad (n \geq 2) \quad (16)$$

The differential characteristics of the aggregation are represented by molar f_n and weight w_n distribution functions of aggregates, molar f_{mon} , f_{lin} , f_{cycl} , and weight w_{mon} , w_{lin} , w_{cycl} fractions of monomers, linear and cyclic structures, the fractions f_{OH} of free OH groups, and distribution functions f_{HB} , namely, $f_{\text{HB},0}$ is a part of monomer alcohol molecules, and $f_{\text{HB},1}$, $f_{\text{HB},2}$ are parts of alcohol molecules participating in one and two H bonds accordingly:

$$f_n = \frac{c_{B_n}}{c_{\text{sum},B}}, \quad f_{\text{mon}} = \frac{c_b}{c_{\text{sum},B}}, \quad f_{\text{lin}} = \frac{\sum_{n=2}^{\infty} \sum_{l=1}^2 c_{B_{n,l}}}{c_{\text{sum},B}} = \frac{\sum_{n=2}^{\infty} c_{B_n}}{c_{\text{sum},B}}, \quad f_{\text{cycl}} = \frac{c_{B_{4,\text{cycl}}}}{c_{\text{sum},B}} \quad (17)$$

$$w_n = \frac{nc_{B_n}}{c_B^0}, \quad w_{\text{mon}} = \frac{c_b}{c_B^0}, \quad w_{\text{lin}} = \frac{\sum_{n=2}^{\infty} \sum_{l=1}^2 nc_{B_{n,l}}}{c_B^0} = \frac{\sum_{n=2}^{\infty} nc_{B_n}}{c_B^0}, \quad w_{\text{cycl}} = \frac{4c_{B_{4,\text{cycl}}}}{c_B^0} \quad (18)$$

$$f_{\text{OH}} = \frac{\sum_{n=1}^{\infty} c_{B_n}}{c_B^0} = \frac{c_b + \frac{2Kc_b^2}{1 - K'c_b}}{c_B^0}, \quad f_{\text{HB},0} = w_{\text{mon}} = \frac{c_b}{c_B^0}, \quad f_{\text{HB},1} = \frac{2\sum_{n=2}^{\infty} c_{B_n}}{c_B^0} = \frac{4Kc_b^2}{(1 - K'c_b)c_B^0} \quad (19)$$

$$f_{\text{HB},2} = \frac{\sum_{n=3}^{\infty} (n-2)c_{B_n} + 4c_{B_{4,\text{cycl}}}}{c_B^0} = \frac{2K'c_b^2Kc_b}{(1 - K'c_b)^2c_B^0} + \frac{4c_{B_{4,\text{cycl}}}}{c_B^0} \quad (20)$$

The relation between the structure of the mixture and its permittivity ϵ_s can be expressed by using dipole correlation factors for the solution g_s^d and that for the components g_A^d , g_B^d .^{1-6,44-46}

$$g_s^d = \frac{9k_B T \sum_{i=1}^k x_i^0 V_{m,i} \left[\frac{(\epsilon_s - \epsilon_{\infty,i})}{(2\epsilon_s + \epsilon_{\infty,i})} \right]}{4\pi N_0 \epsilon_s \sum_{i=1}^k x_i^0 \mu_i^2 \left[\frac{(\epsilon_{\infty,i} + 2)}{(2\epsilon_s + \epsilon_{\infty,i})} \right]^2} = \frac{\sum_{i=1}^k g_i^d x_i^0 \mu_i^2 \left[\frac{(\epsilon_{\infty,i} + 2)}{(2\epsilon_s + \epsilon_{\infty,i})} \right]^2}{\sum_{i=1}^k x_i^0 \mu_i^2 \left[\frac{(\epsilon_{\infty,i} + 2)}{(2\epsilon_s + \epsilon_{\infty,i})} \right]^2} \quad (21)$$

where $\epsilon_{\infty,i}$, μ_i are the deformation permittivity and dipole moment of the i th component respectively, N_0 is the Avogadro number, and k_B is the Boltzmann constant. Equation 21⁴⁵⁻⁴⁷ presents the generalization of the Frohlich approach⁴⁸ to mixtures of polar substances and it allows analyzing the permittivity of those in the whole composition range. For extracting deformation polarization at the derivation of eq 21, the model approach was used

The correlation factor for the solution g_s^d and for components g_A^d and g_B^d can be determined both from experimental data and from a model of supramolecular structure. It should be underlined that the values g_s^d , g_A^d , and g_B^d include correlations of both similar and differing components of the mixture. The permittivity is a basic property for structural analysis because, in contrast with thermodynamic properties, it is directly related to the structure of supramolecular species.^{1-6,45-47}

The dipole moments of cyclohexane and ethanol molecules were chosen $\mu_a = 0$ D and $\mu_b = 1.66$ D respectively.⁴⁹ The molar deformation polarizations of the components $P_{\infty,A} = 27.50$ cm³/mol (cyclohexane) and $P_{\infty,A} = 14.48$ cm³/mol (ethanol), which are required for calculating the deformation permittivities of the pure liquids $\epsilon_{\infty,A}$ and $\epsilon_{\infty,B}$ by using the Clausius–Mossotti equation,²⁵ were determined by the bond additivity method.⁵⁰

There were some previous attempts to derive a theoretical expression for the correlation factor of pure alcohol in the framework of the chainlike model of aggregation (e.g., refs 51–54). The results obtained were based on quite crude assumptions concerning the structure of aggregates as well as the model of aggregates mixture. It was assumed that aggregates of alcohol have infinite length,^{51,52} and the rotation around H bonds in aggregates is an unhindered one.⁵¹⁻⁵³ In ref 54, at calculating dipole moments of aggregates, some additional assumptions were made. The aggregate's mixture were considered as ideal.^{53,54} Some special results were obtained also for the correlation factor of liquid hydrogen fluoride⁵⁵ and *N*-amides.^{56,57}

In ref 58, the general equations were derived for the dipole correlation factor of liquids with chainlike aggregation, which were applied to alcohols in refs 42 and 43 (see also ref 59). H bonding of alcohol molecules by two ways in aggregates due to two lone-pair electrons on the oxygen atom of the molecule was taken into account. Thus new types of topologically linear chainlike aggregates due to H bonding were revealed.

The relationships for dipolar correlation factors of mixtures g_s^d , g_A^d , and g_B^d in eq 21 were obtained in ref 46. The model of chainlike aggregation developed in ref 46 includes aggregates of arbitrary length and composition. The results obtained in ref 46 were extended in ref 40 to liquid and mixtures with both chainlike and cyclic aggregates. Recently, the model, which includes both chainlike and branched comblike aggregates of alcohol, was developed.^{60,61} In general, these equations relate permittivity and dipole correlation factor with the structure of supramolecular species and thermodynamics of their formation. Therefore, the relationships derived allow quantitative analysis of the permittivity and dipole correlation factor of mixtures in the whole concentration range for wide spectra of the aggregation models. The previous works on analysis of dielectric permittivity of mixtures (e.g., refs 21, 30, and 62–73) discussed the nature of alcohol aggregation, mainly in the limited mixture composition ranges, and were based on primitive models for mixture permittivity. The equations for the dipole correlation factor both liquids and mixtures as well as the results of using those were reviewed in refs 1–6, 40, and 46.

For the model of the mixture presented in this work, which includes both chainlike and cyclic aggregation of ethanol, the

TABLE 1: Concentration “Equilibrium Constants” K , K' , and $K_{4,\text{cycl}}$ of Cyclohexane–Ethanol Solution (x_B^0 : Ethanol Mole Fraction)

x_B^0 , mole fraction T , K	0.2	0.4	0.6	0.8	1.0
K					
283.15	10.7	7.74	6.45	5.86	5.56
293.15	7.81	5.80	4.85	4.41	4.20
298.15	6.72	5.07	4.24	3.89	3.68
303.15	6.01	4.51	3.76	3.41	3.23
323.15	3.60	2.70	2.33	2.12	2.01
338.15	2.66	2.03	1.71	1.55	1.46
K'					
283.15	49.6	36.8	30.1	28.4	27.0
293.15	33.2	25.2	21.2	19.5	18.6
298.15	27.5	20.9	17.8	16.2	15.4
303.15	23.8	18.2	15.4	14.0	13.3
323.15	14.0	11.0	9.40	8.60	8.16
338.15	9.49	7.64	6.51	5.92	5.61
$K_{4,\text{cycl}}$					
283.15	9.99×10^5	1.77×10^5	6.61×10^4	3.95×10^4	2.98×10^4
293.15	3.01×10^5	5.81×10^4	2.05×10^4	1.26×10^4	9.38×10^3
298.15	1.41×10^5	2.95×10^4	1.15×10^4	6.74×10^3	5.00×10^3
303.15	7.12×10^4	1.51×10^4	5.70×10^3	3.37×10^3	2.52×10^3
323.15	8.33×10^3	1.90×10^3	7.60×10^2	4.56×10^2	3.35×10^2
338.15	1.87×10^3	5.40×10^2	2.10×10^2	1.21×10^2	8.74×10^1

TABLE 2: Thermodynamic Functions of Aggregation for Pure Ethanol (ΔG_{298} , ΔH : kJ/mol; ΔS : J/(mol·K))

ΔG_{298}	ΔH	ΔS	$\Delta G'_{298}$	$\Delta H'$	$\Delta S'$	$\Delta G_{4,\text{cycl},298}$	$\Delta H_{4,\text{cycl}}$	$\Delta S_{4,\text{cycl}}$
-2.9 ± 0.1	-19 ± 3	-54 ± 6	-6.8 ± 0.1	-22 ± 3	-51 ± 5	-22 ± 0.1	-86 ± 8	-216 ± 24
$\Delta G_{298,v}$	ΔH_v	ΔS_v	$\Delta G'_{298,v}$	$\Delta H'_v$	$\Delta S'_v$	$\Delta G_{4,\text{cycl},298,v}$	$\Delta H_{4,\text{cycl},v}$	$\Delta S_{4,\text{cycl},v}$
-10 ± 0.1	-20 ± 1	-34 ± 1	-14 ± 0.1	-23 ± 2	-30 ± 5	-42 ± 0.4	-88 ± 8	-154 ± 25

correlation factor of solution g_s^d can be derived from the more general expressions that are given elsewhere:^{3,40,46}

$$g_s^d = g_B^d = 1 + \frac{4Kc_b^2}{c_B^0 \mu_b^2 (1 - K'c_b)^2} \tilde{\mu}_b \langle \mathbf{T}_{bb}^{(1)} \rangle \cdot (\mathbf{E}_3 - K'c_b \langle \mathbf{T}_{bb}^{(1)} \rangle)^{-1} \mu_b - \frac{4K_{4,\text{cycl}}c_b^4}{c_B^0} \quad (22)$$

where $\mu_{a,b}$ are the vector-column of the dipole moment, the sign \sim denotes the transposition of the matrix, \mathbf{E}_3 is the unit matrix of the third order, and matrix $\langle \mathbf{T}_{bb}^{(1)} \rangle$ are given by eq 4. Terms in eq 22 correspond to interrelated contributions from free ethanol molecules, chainlike aggregates of arbitrary size, and from tetramers of ethanol.

Analysis of the Properties of Solutions

The model of structure of pure ethanol, which takes into account only chain alcohol aggregates, was developed earlier⁴² and it was applied to describe the permittivity of pure ethanol in the temperature range 233–473 K.⁴³ In ref 43, the equilibrium constants of ethanol aggregation K , K' and structural parameters in matrixes $\langle \mathbf{T}_{bb}^{(1,2)} \rangle$ (eq 4) were determined. It was shown⁴³ that this model is quite appropriate for the dielectric properties of pure ethanol in a wide temperature range.

However, in solutions of alcohol in nonpolar and low-polar solvents, according to the QCNAS model,^{1–6,44} relative stability of low-polar cyclic alcohol aggregates increases. In the present work, the model⁴² was extended to include cyclic association of ethanol. This advanced model of alcohol proved to be adequate to describe thermodynamic and dielectric properties of alcohol solutions both in nonpolar (1,4-dioxane,^{14,15} tetrachloromethane^{16,17}) and polar (propanone¹⁸) solvating solvents.

However, it should be underlined that the behavior of the thermodynamic and dielectric properties of the mixture cyclohexane–ethanol is more complicated in comparison with above-mentioned mixtures, and thus it was necessary to improve essentially the method of analysis of the data proposed earlier.

In this paper, the ethanol dimerization constant K (eq 3) and structural parameters of aggregation were taken from ref 43. The equilibrium constant of formation of cyclic nonpolar ethanol aggregates $K_{4,\text{cycl}}$ (eq 3) was obtained by fitting to dipole correlation factor g_s^d of cyclohexane–ethanol solution in the concentration range $x_B^0 = 0.0$ – 0.2 mole fraction and $x_B^0 = 1$ mole fraction. Accordingly, the equilibrium constant of formation of higher ethanol aggregates ($n \geq 3$) K' (eq 3) was refit simultaneously. Concentration equilibrium constants K , K' , and $K_{4,\text{cycl}}$ are given in Table 1 as functions of concentration and temperatures. The thermodynamic functions of aggregation: Gibbs energy, enthalpy, and entropy of dimerization (ΔG_{298} , ΔH , ΔS), formation of higher linear aggregates ($n \geq 3$) ($\Delta G'_{298}$, $\Delta H'$, $\Delta S'$), and cyclic ($\Delta G_{4,\text{cycl},298}$, $\Delta H_{4,\text{cycl}}$, $\Delta S_{4,\text{cycl}}$) ethanol aggregates are given in Table 2. Thus, in fact, this model includes just one additional adjustable parameter, namely, the equilibrium constant of the cyclic aggregation of ethanol, obtained from analysis of permittivity.

Thermodynamic functions of aggregation were also calculated by using concentration equilibrium constants defined as follows^{1–6, 40,41}

$$K_v = \frac{c_{B_2}}{c_b c_b V_{m,B}}, \quad K'_v = \frac{c_{B_{n+1}}}{c_{B_n} c_b V_{m,B}}, \quad n \geq 2; \quad K_{4,\text{cycl},v} = \frac{c_{B_4}}{c_b^4 V_{m,B}} \quad (23)$$

This function corresponds to the standard states of monomers

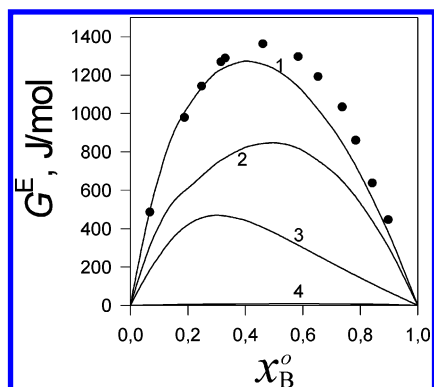


Figure 1. Excess Gibbs energy G^E in the cyclohexane–ethanol mixtures at $T = 298$ K. Points, experimental data;²² solid lines, values calculated by QCNAS: 1, total values, 2, association contribution, 3, dipole contribution, 4, dispersion contribution; x_B^o : ethanol mole fraction.

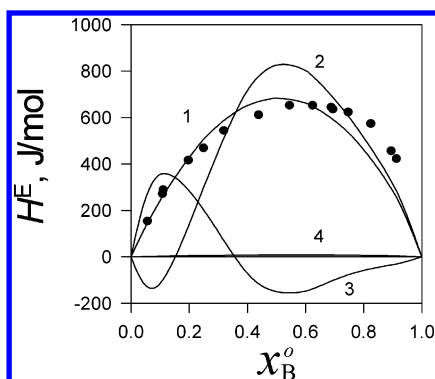


Figure 2. Excess enthalpy H^E in the cyclohexane–ethanol mixtures at $T = 298$ K. Points, experimental data;²⁰ solid lines, values calculated by QCNAS: 1, total values, 2, association contribution, 3, dipole contribution, 4, dispersion contribution; x_B^o : ethanol mole fraction.

or aggregates defined as pure hypothetical liquids,^{1–3} and therefore, it may be expected that they give more adequate parameters of aggregation having transparent physical meaning.

Activity coefficients of components and excess Gibbs energy of solutions were calculated by using parameters obtained by the analysis of dielectric properties without additional fitting. Excess enthalpy H^E and entropy S^E were calculated by using general thermodynamic relationships.²⁵

Results and Discussion

The data obtained show that the major contribution to excess Gibbs energy G^E and enthalpy H^E (Figures 1 and 2) and activity coefficients of components γ_A and γ_B (Figure 3) is due to specific interactions, for instance, contribution of specific interactions to G^E is up to $\sim 65\%$ ($T = 293$ K). The contributions due to dipole and dispersion interactions to excess functions G^E and H^E are much less, and increase as temperature rises. Dipole contribution to G^E is $\sim 30\%$ ($T = 293$ K), while dispersion contribution is negligible. The contribution of nonspecific interactions to excess entropy S^E (Figure 4) is more than that to G^E and H^E and is comparable with the contribution of specific interactions. Therefore, contribution of aggregation to S^E is quite important for this mixture. The deviation between calculated and experimental values of activity coefficients γ_A and γ_B and excess functions G^E , H^E , and S^E amounts to $\sim 10\%$. Thus, the model developed allows description of both thermodynamic functions of mixing and, therefore, the vapor–liquid equilibrium of cyclohexane–ethanol mixture in a whole com-

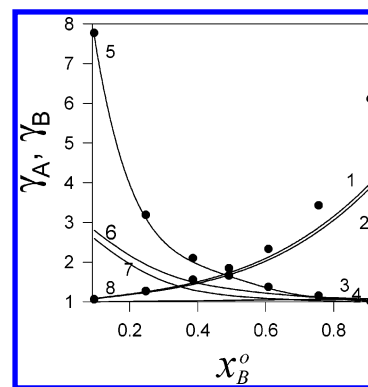


Figure 3. Activity coefficients γ_A , γ_B in the cyclohexane–ethanol mixtures at $T = 293$ K. Points, experimental data;¹⁹ solid lines, values calculated by QCNAS: 1, γ_A , total values, 2, γ_A^{ass} , association contribution, 3, γ_A^{dip} , dipole contribution, 4, γ_A^{dis} , dispersion contribution; 5, γ_B , total values, 6, γ_B^{ass} , association contribution, 7, γ_B^{dip} , dipole contribution, 8, γ_B^{dis} , dispersion contribution; x_B^o : ethanol mole fraction.

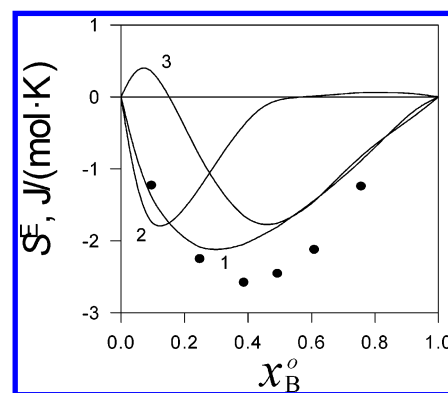


Figure 4. Excess entropy S^E in the cyclohexane–ethanol mixtures at $T = 298$ K. Points, experimental data;²⁰ solid lines, values calculated by QCNAS: 1, total values, 2, association contribution, 3, dipole contribution; x_B^o : ethanol mole fraction.

position range and in a wide temperature range from the molecular picture of the supramolecular organization of the mixture. It is necessary to note, despite the contribution of nonspecific interactions to excess thermodynamic functions, the account of nonspecific interactions is important both for description of thermodynamic nonideality of solutions in general and especially for the aggregation parameters due to essential dependence of concentration “equilibrium constants” on the mixture composition (Table 1).

The permittivity ϵ_s and dipole correlation factor g_s^d are also satisfactorily described by the proposed model with deviations about 4% and 10%, respectively (Figures 5 and 6). Formation of nonpolar cyclic ethanol aggregates results in a minimum of dipole correlation factor $g_s^d < 1$ in dilute ($x_B^o < 0.2$ mole fraction) alcohol solutions with low values of permittivity. This is in contrast to the mixtures of alcohols with 1,4-dioxane^{14,15} and propanone,¹⁸ where there is no minimum of g_s^d at dilute alcohol mixtures. Positive deviations of dipole correlation factor from unity at concentration range $x_B^o = 0.2–1.0$ mole fraction are due to preferable parallel-like orientation of the dipole moments of molecules in chain alcohol aggregates, which prevail in solution in this composition range. It should be underlined that the dipole correlation factor is much more sensitive to supramolecular structure of solution in comparison with permittivity.

The data on the equilibrium constants of the aggregation allow us to obtain unique information both on the integral and

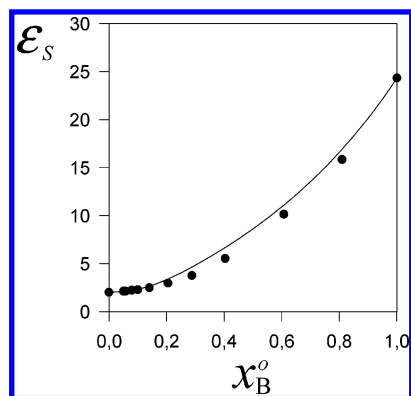


Figure 5. Permittivity ϵ_s in the cyclohexane–ethanol system at 298 K. Points, experimental data;²¹ line, values calculated by QCNAS; x_B^o : ethanol mole fraction.

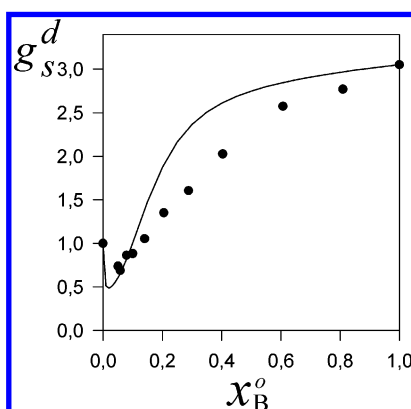


Figure 6. Dipole correlation factor g_s^d in the cyclohexane–ethanol system at 298 K. Points, experimental data;²¹ line, values calculated by QCNAS; x_B^o : ethanol mole fraction.

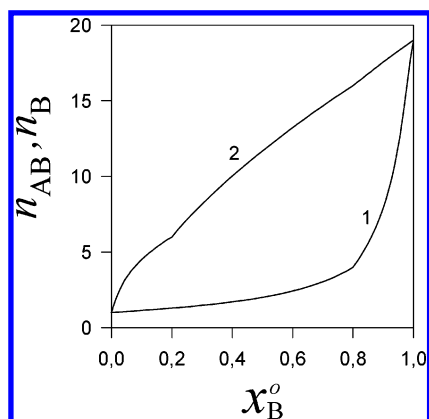


Figure 7. Average degree of aggregation of solution n_{AB} and alcohol n_B (line 2) in cyclohexane–ethanol mixtures at 298 K; line 1, n_{AB} , line 2, n_B ; x_B^o : ethanol mole fraction.

differential parameters of the supramolecular organization in the mixture investigated. It should be underlined that most of these data on structural features of the supramolecular ordering on mixtures are difficult or impossible in general for obtaining by other techniques due to the principal limitations.^{1–6} Nevertheless, the data obtained were compared where it was possible with those obtained from different experimental and modeling techniques.

The degree of aggregation of pure ethanol \bar{n}_B approaches 20 at 298 K (Figure 7). This is evidence of large nanosize supramolecular aggregation in concentrated alcohol solutions.^{1–6} This conclusion is in agreement with the results obtained from

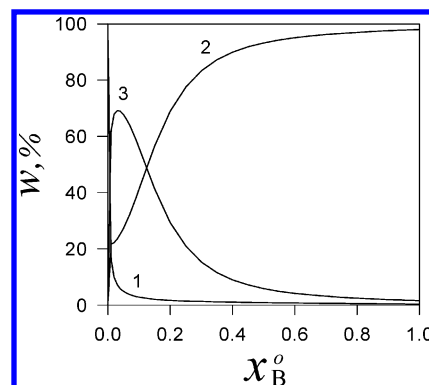


Figure 8. Weight fractions w of alcohol monomers (line 1), linear aggregates (line 2), and cyclic tetramers (line 3) in cyclohexane–ethanol mixtures at 298 K, x_B^o : ethanol mole fraction.

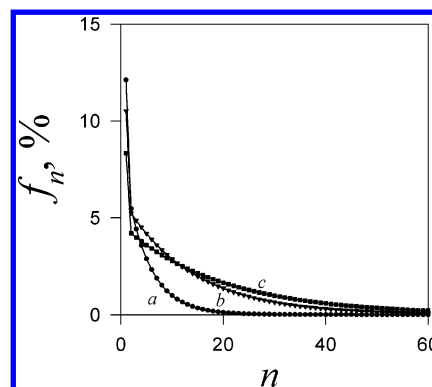


Figure 9. Distribution function of aggregates f_n in cyclohexane–ethanol mixtures at 298 K, $x_B^o = 0.1$ (a), 0.5 (b), 0.9 (c)

diffraction data concerning the mean oxygen–oxygen coordination numbers, corresponding to O–H...O bonding in liquid ethanol.^{34,35}

The functions describing distribution of aggregates according to their size and structure are shown in Figure 8, where weight fraction w_{mon} , linear w_{lin} , and cyclic w_{cycl} ethanol aggregates are presented. A fraction of cyclic aggregates goes through the maximum in dilute ethanol solutions ($w_{\text{cycl}} \sim 70\%$, $x_B^o = 0.1$ mole fraction, $T = 298$ K) and dramatically decreases as alcohol concentration rises. In pure alcohol, the role of cyclic aggregates is much less essential, $w_{\text{cycl}} \sim 1\%$ ($T = 298$ K). Therefore, cyclic tetramers play an essential role only in dilute alcohol solutions at $x_B^o < 0.2$ mole fraction, where their fraction is maximal. Thus, the model of chainlike aggregation is a good initial approach for pure ethanol and in mixtures rich in ethanol. These dependencies are due to much faster decrease of the concentration equilibrium constant for the forming of cyclic alcohol aggregates in comparison with those for chainlike association (Table 1) because the stability of the polar ethanol aggregates is increasing with permittivity of the mixture. The weight fraction of monomer molecules w_{mon} for pure ethanol is in good agreement with that estimated by Monte Carlo³⁹ and molecular dynamics (MD)⁷⁴ simulations.

The more detailed picture of supramolecular organization of the mixtures under analysis is given by the molar f_n and weight w_n distribution functions of aggregates, the fraction of monomer alcohol molecules $f_{\text{HB},0}$, and alcohol molecules taking part in one $f_{\text{HB},1}$ and two $f_{\text{HB},2}$ H bonds and the fraction of free OH groups f_{OH} (Figures 9–12). The molar distribution function of aggregates f_n (Figure 9) decreases monotonically, and the weight distribution function of aggregates w_n (Figure 10) has a maximum as the mixture composition changes. The increase

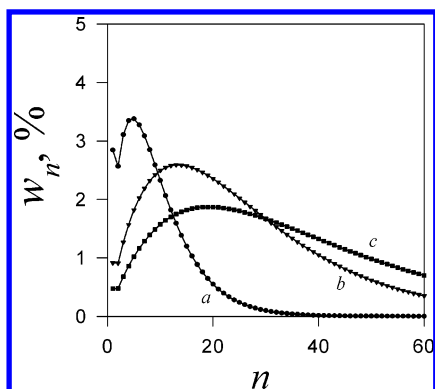


Figure 10. Distribution function of aggregates w_n in cyclohexane–ethanol mixtures at 298 K, $x_B^0 = 0.1$ (a), 0.5 (b), 0.9 (c).

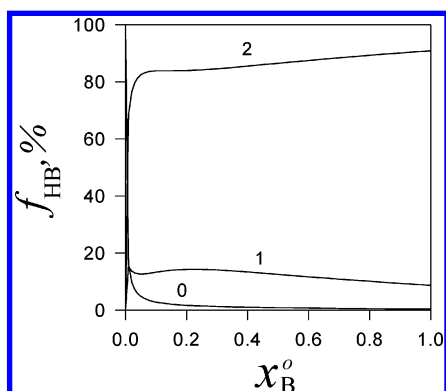


Figure 11. Distribution function f_{HB} of monomer ethanol molecules (line 0) and ethanol molecules taking part in 1 (line 1) and 2 (line 2) H bonds in cyclohexane–ethanol mixtures at 298 K; x_B^0 : ethanol mole fraction.

TABLE 3: Distribution Function of Monomer Ethanol Molecules, $f_{HB,0}$, and Ethanol Molecules Taking Part in 1, $f_{HB,1}$, and 2, $f_{HB,2}$, (%) H Bonds in Pure Ethanol at Room Temperature

ref	$f_{HB,0}$	$f_{HB,1}$	$f_{HB,2}$	$f_{HB,3}^a$
Jorgensen ⁷⁵	2.2	14.7	78.4	4.4
Saiz et al. ⁷⁶	1	14	80	5
González et al. ⁷⁷	1.1	13.6	80.2	5.1
this work	0.36	7.91	91.72	

^a The model presented in this work does not imply ethanol molecules taking part in three H bonds (see refs 60, 61).

of alcohol concentration leads to smoother dependence of these distribution functions.

The fraction of alcohol molecules taking part in two H bonds $f_{HB,2}$ (Figure 11) at $T = 298$ K is maximal and essentially exceeds the fraction of monomer molecules $f_{HB,0}$ and molecules of alcohol participating in one H bond $f_{HB,1}$, and increases as alcohol concentration increases. The fraction of molecules $f_{HB,1}$ (Figure 11) representing terminal molecules in aggregates approaches ~12–15% in pure ethanol ($T = 298$ K), and weakly depends on concentration of solution. The fraction of free molecules of ethanol $f_{HB,0}$ (Figure 11) dramatically decreases as alcohol concentration increases and approaches ~1% ($T = 298$ K) in the pure alcohol. These values are in good agreement with the results of MD simulation of pure ethanol⁵¹ (Table 3).

The fraction of free OH groups f_{OH} (Figure 12) sharply falls in dilute solutions, approaching ~10% at $x_B^0 = 0.05$ ($T = 298$ K), and weakly decreases at further increasing of alcohol concentration. The f_{OH} fraction in pure ethanol is equal to ~4%

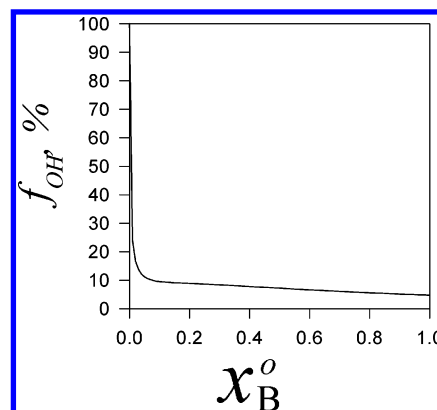


Figure 12. Fractions f_{OH} of free OH groups at 298 K, x_B^0 : ethanol mole fraction.

TABLE 4: Fractions of Free OH groups f_{OH} (%) in Pure Ethanol

T , K	293.15	342.15	ref
f_{OH}	2.9 3.8	6.9 7.9	Luck ²⁷ this work

($T = 293$ K), ~4.5% ($T = 298$ K), and ~6% ($T = 318$ K). These values are in good agreement with the spectroscopic data²⁷ (Table 4).

It can be concluded from the performed analysis that the proposed model shows a good performance in the simultaneous description of both thermodynamic and dielectric properties of the cyclohexane–ethanol solutions with complex supramolecular organization in the whole composition range. The model assuming both chain and cyclic aggregation of alcohol allows us to obtain new data about supramolecular organization of cyclohexane–ethanol mixture and their structural and thermodynamic parameters. The results show that a relatively low fraction of cyclic nonpolar alcohol aggregates essentially influences the properties of cyclohexane–ethanol solution as a whole and, in particular, dielectric properties of dilute solutions. The role of cyclic alcohol structures increases as ethanol concentration decreases. In concentrated solutions and in pure alcohol, chain alcohol aggregates are predominant. Therefore, a simultaneous account of linear and cyclic alcohol aggregation is necessary for a description of supramolecular organization of cyclohexane–ethanol solutions as well as similar systems within the whole concentration range and its influence on the physicochemical properties of these systems on the molecular-structural level. It should be underlined that the model proposed includes in fact just one fitting parameter.

Thus, the methods developed allow us to obtain new data on the supramolecular organization in mixtures. They give the possibility of describing different macroscopic properties of the cyclohexane–ethanol mixture from the molecular-based model, taking into account the supramolecular structure of the mixture. It should especially be underlined the possibility to study long-range molecular correlations beyond the first coordination shells because this information is difficult or impossible to derive from other techniques.^{1–6}

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