

## Models of liquid mixtures: Structure, dynamics, and properties\*

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*Abstract:* Models of the structure and properties of liquid mixtures are outlined. The main focus is on quasicheical models for the modeling of supramolecular ordering in mixtures, self-organized by H-bonds, leading to a unified description of their physicochemical properties. Models of polyvariable supramolecular species are discussed with respect to structure and composition of the mixtures, taking into account the cooperativity of H-bonding, and leading to a description of electric (dipole moment) and optic (polarizability) properties. We analyze the interrelations of thermodynamic functions (Gibbs energy, enthalpy, entropy), dielectric (permittivity) and optical properties (refractive index and its fluctuation derivatives, defining Rayleigh light scattering) of nonideal mixtures as well as the microscopic characteristics of the aggregates. Methods are developed in order to obtain both integral and differential parameters of aggregation. Models for the description of supramolecular reorganization, intramolecular transitions, and energy transfer during molecular thermal motion as well as fluctuation and relaxation phenomena are considered. Applications both to liquids and mixtures are outlined. The supramolecular assemblies in liquids with long-range molecular correlations are established. Macroscopic manifestations of the supramolecular organization in the properties of liquids are characterized.

### INTRODUCTION

The development of the theory of liquids is based upon investigations of their structure, of the molecular interactions, and the dynamic processes of the molecular thermal motion. Successful investigations of liquids are based on combinations of experimental techniques, and theoretical approaches based on general concepts are required for their evaluation. This is also true if one wants to attempt the molecular design of liquid materials.

There has been recently an increasing interest in studies of aggregation due to noncovalent intermolecular forces and their manifestations in macroscopic properties of a matter. The aggregation phenomena are important for phase transitions, glass formation, nucleation etc.; they are related to interdisciplinary fields of science like the theory of self-organization of matter and synergetics [1,2]. Understanding this phenomenon is also required if one wants to construct devices based on the microscopic properties of aggregates. Progress has been achieved here for crystal solids where structure and properties of aggregates may be characterized quite definitely [3].

The situation for liquids is much more complicated due to the temporal mobility of the structure during molecular thermal motions. Furthermore, the structure changes markedly under variations of thermodynamic conditions. The main focus is on local ordering inside the nearest coordination shells,

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and the role of long-range molecular correlations, both for the structure and the properties of liquids, is in general not fully recognized.

Molecular liquids, however, are favorable objects for detailed studies of aggregation phenomena. The structural and dynamic features of aggregation in molecular liquids represent the elementary steps for more complex systems: hierarchically, this includes liquid crystals, polymers, micelles and micro-emulsions, colloids, etc. Mixtures where hydrogen bonds are present (they are the attractive directed interactions intermediate between chemical bonds and van der Waals forces) are particularly attractive objects for studies of supramolecular ordering and the structure and composition of aggregates [4–9].

## DESCRIPTION OF LIQUID STRUCTURE

Among the principal approaches for the modeling of mixture, the statistical–mechanical theory and simulation methods should be mentioned first. There, the physical language, based on the notion of correlation functions  $F_s$  ( $s = 2, 3, \dots, N$ ) defining the probabilities of the spatial configurations of particles, is applied [10,11]. A binary function,  $F_2(R) = g(R)$ , occupies a central role because, firstly, the thermodynamic functions can be expressed in terms of this function and, secondly, it can be studied by diffraction techniques.

Many approaches have been proposed for calculating these radial function, e.g., the Born–Bogolubov–Green–Kirkwood–Ivon chain of equations, the Ornstein–Zernicke equation (Percus–Yevick and hyperchain equations corresponding to different closures), and then perturbation theory, etc. [10]. In simulation such as the molecular dynamics and the Monte Carlo methods the correlation functions are routinely computed as a way to present the simulation data [11].

Radial functions  $g(R)$  give a one-dimensional picture of the liquid's structure. Diffraction techniques allow us to study this function for the nearest molecules, reflecting thus only the local order; long-range molecular correlations remain in the shadow. In computer simulation, due to the periodic boundary conditions and the limited computer time, the long-range correlations may be cut off artificially. Thus, in contrast with crystalline solids, the role of supramolecular ordering in liquids is certainly not fully understood.

Different approaches are used for complex liquids, and especially for those with H-bonds [4–8,12]. The first ones are physical statistical–mechanical models, e.g., SAFT (statistical associated fluid theory) [13], based on Wertheim's perturbation theory; secondly, the lattice models, founded on Guggenheim–Barker theory [14], and its further modifications, e.g., LFHB (lattice fluid hydrogen bond) [15], and finally the chemical ones, combining extensions of hard sphere approaches for anisotropic particles with equations for chemical equilibria [12]. The main areas where these approaches [12–15] are used are the equations of state and thermodynamic functions of mixing. Presently, these approaches cannot describe other properties such as dielectric or optical ones, more directly related with supramolecular ordering of mixtures.

## QUASICHEMICAL MODELS

In chemistry, the concept of concentrations of particle and reactions between them is applied. In the quasichemical models, the material processes are represented by the equations of chemical reaction:



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

where  $M_i$  designates the  $i$ -th reagent, and  $v_{i\alpha}$  and  $v'_{i\alpha}$  are the stoichiometric coefficients of one in the reaction  $\alpha$ . These processes are characterized by the extent (or degree of advancement)  $\xi_\alpha$  and the affinity  $A_\alpha$  (eq. 2), where  $\mu_i$  is the chemical potential of the  $i$ -th reagent, and rate constants  $k_\alpha, k'_\alpha$ . For non-equilibrium states, the extents are independent parameters, and the corresponding affinities are not equal to zero.

The extents  $\{\xi_\alpha\}$  (eq. 2) represent scalar internal variables. The vectors of internal variables represent, e.g., fluctuating local velocities or polarizations. Tensor variables are entered in order to describe anisotropic states of a system; examples of mechanic ones are 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 those generally are not reduced to mechanic ones. The concept of internal variables is especially important for the theory of irreversible processes.

A quasichemical model combines both macroscopic and molecular theory. It can be treated as an extension of chemical thermodynamics and kinetics to the treatment of processes in matter, e.g., spatial reorganizations of intermolecular structures (in particular, the association processes) 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 (eq. 1) and to derive equations for physicochemical properties. The term "quasichemical" underlines that the description uses a chemical language for a wide spectra of processes that, in general, do not entail changes in the chemical nature of the reagents. Thus, quasichemical models provide the language for studying both equilibrium and kinetic properties of liquids and allow us to present results for many phenomena in common terms [4–8].

Quasichemical models of association processes have been applied in several instances to thermodynamic and spectroscopic properties of liquid systems [4–8,16–18]. Recently, along with the elaboration of association models and the thermodynamics of associated solutions, this approach has been extended to dielectric, optic, and kinetic properties of mixtures. Among the properties considered are thermodynamic functions, the Gibbs energy  $G$ , enthalpy  $H$ , entropy  $S$ , and the corresponding excess functions for mixtures,  $G^E, H^E, S^E$ , the activity coefficients of the components  $\gamma_A, \gamma_B$ , the dielectric permittivity  $\epsilon_S$ , and optical properties such as Rayleigh ratios for isotropic and anisotropic light scattering  $R_{is}$  and  $R_{an}$ , defined by different molecular parameters. Applications concerning molecular interactions, thermodynamics of aggregation and the structure of aggregates have been discussed [6–8].

We have now to identify the next interrelated problems for the description of supramolecular ordering and the properties of liquid mixtures in the quasichemical approach [4–8]: First, we have to describe the structure, composition, electric, and optical properties of the aggregates themselves; secondly, the thermodynamics of aggregate mixture must be developed; and thirdly, the equations for the macroscopic properties of liquids must be derived. The topological features of the aggregate (the most typical of them are linear, cyclic, star-, comb, tree-like, and net-like) should be taken into account.

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 on any site of an aggregate any molecule from the mixture components may be located. Different ways of bonding lead to the structural multivariance of the aggregates. Starting from the "root" molecule, various ways for further aggregate growth are possible. Thus, both structural and compositional multiformity of aggregates leads to new types of aggregate structure. For instance, even for chain-like aggregates of homogeneous composition, new structures were established.

The models 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 by introducing different equilibrium constants for dimerization and the formation of higher aggregates. More complicated types of cooperativity were then established and matrix techniques were developed [4–8] both for microscopic properties of aggregates and the corresponding macroscopic ones.

The polyvariability of aggregates concerning the structure and the composition gives the possibility to study systems self-organized by noncovalent directed interactions like H-bonds, conserving the information in double or more multivalent forms. Thus, controlling both the compositional and structural reorganization of supramolecular aggregates allows for molecular information processing in general, especially in the living nature [4–8].

## QUASICHEMICAL MODELS IN THERMODYNAMICS OF MIXTURES

The thermodynamic model for mixture of aggregates is the first step toward relating macroscopic properties of mixture with microscopic properties of aggregates. The approach for the contributions by molecular interaction to the thermodynamic functions of mixtures was developed, and the quasicheical nonideal associated solution (QCNAS) model has been constructed [4–8].

The activity coefficients of component  $\gamma_A$ ,  $\gamma_B$  and the excess functions of mixture, e.g., the excess enthalpy  $H^E$ , include three, generally related, contributions: first, the association, describing the deviations from ideality due to repulsion forces and association, second, a contribution due to dispersion interactions, and third, one due to dipolar forces:

$$\gamma_{A,B} = \gamma_{A,B}^{ass} \gamma_{A,B}^{dis} \gamma_{A,B}^{dip}, H^E = H^{E,ass} + H^{E,dis} + H^{E,dip} \quad (3)$$

The first terms in eq. 3,  $\gamma_{A,B}^{ass}$ , are related with the average numbers of association in individual liquids  $A$  and  $B$ ,  $\bar{n}_A$ ,  $\bar{n}_B$  and in solution  $n_{AB}$ , representing the integral parameters of aggregation. The differential parameters of the aggregation are given, e.g., by molar,  $f_n$ , and weight,  $w_n$ , distributions, which give the fractions of the aggregates consisting of  $n$  molecules, and molecules, included in those, respectively.

The estimation of both dispersion  $\gamma_{A,B}^{dis}$  and dipolar  $\gamma_{A,B}^{dip}$  contributions to the activity coefficients (eq. 3) is important for extracting the contributions due to aggregation  $\gamma_{A,B}^{ass}$ . The thermodynamic non-ideality of the aggregate mixture leads to a dependence of the “equilibrium constants”, expressed by the molar concentrations, on the solution composition. This is highly important for studying the aggregation.

The multivariance of associates with respect to composition and structure results to different dependencies of the excess functions on solution composition, but the influence of those on the thermodynamic functions is essential only if there is a difference in the stoichiometry of association. Thermodynamic functions do not include directly the structural features of aggregates and thus, for instance, models with the same stoichiometry and different structure of aggregates, e.g., linear and cyclic ones, cannot be discriminated by thermodynamic studies.

## QUASICHEMICAL MODELS IN DIELECTROMETRY OF MIXTURES

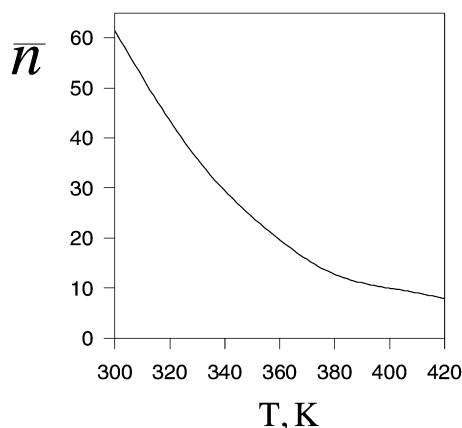
Considerations on the dielectric constant to study the supramolecular organization of liquids are based both on the models for mixture of associated species and on the theory of dielectric properties. For the permittivity  $\epsilon_s$  of the mixture, eq. 4 was derived [4–9]:

$$\frac{9k_B T V_m}{4\pi N_A \epsilon_s} \sum_{j=1}^k \left( \frac{\epsilon_s - \epsilon_{\infty j}}{2\epsilon_s + \epsilon_{\infty j}} \right) \varphi_j^0 = \sum_{j=1}^k \left( \frac{\epsilon_{\infty j} + 2}{2\epsilon_s + \epsilon_{\infty j}} \right)^2 x_j^0 \mu_j^2 g_j^d = g_s^d \sum_{j=1}^k \left( \frac{\epsilon_{\infty j} + 2}{2\epsilon_s + \epsilon_{\infty j}} \right)^2 x_j^0 \mu_j^2 \quad (4)$$

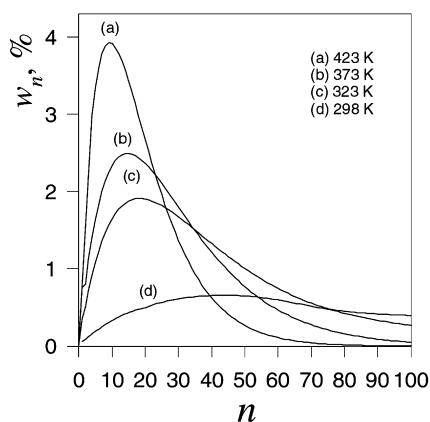
where  $k_B$ ,  $N_A$  are Boltzmann's and Avogadro's constants,  $\epsilon_{\infty j}$ ,  $\mu_j$ , and  $g_j^d = \langle \mu_j \mu_j^* \rangle / \mu_j^2$  are the deformation permittivity, dipole moment, and dipole correlation factor of  $j$ -th component, and  $g_s^d$  is the dipole factor of the solution. Deviations from unity of the dipole factor  $g_s^d$ ,  $g_j^d$  are due to spatial molecular correlations. Relations between the dipole factors  $g_j^d$ ,  $g_s^d$  and the structure of the aggregates and the thermodynamics of their formation have been established [4–8].

Examples [4–8] have demonstrated the fairly reliable discrimination of aggregation models. Models with the same stoichiometry of aggregates and different structures of (e.g., chain-like and cyclic) can be distinguished even qualitatively. New chain-like aggregates were established. Thermodynamic parameters of aggregation, e.g., the equilibrium constants  $K$  of H-bonding, were obtained, and the cooperativity of H-bonding has been revealed.

The long-range correlations by H-bonding founded should be underlined. Average numbers of association  $\bar{n}$  in alkanols are equal to 10 and above at room temperature and increase with decreasing of temperature (Fig. 1). The size distribution functions of aggregate are quite wide, and thus the evidence for larger supramolecular aggregates was established (Fig. 2). Thus, the methods developed allow us to study long-range molecular correlations outside of the nearest coordination spheres.



**Fig. 1** The mean number of association in liquid methanol  $\bar{n}$ .



**Fig. 2** The weight distribution function of aggregates  $w_n$  in liquid methanol.

## QUASICHEMICAL MODELS IN THEORY OF FLUCTUATIONS AND RAYLEIGH LIGHT SCATTERING IN MIXTURES

Rayleigh light scattering is subdivided into isotropic and anisotropic contributions. The isotropic fluctuations of permittivity (refractive index,  $\varepsilon = n^2$ ) and the Rayleigh ratio  $R_{is}$  are usually expressed as sums of terms, interpreted as due to independent fluctuations of temperature, density, and concentration [19]:

$$R_{is} \sim \langle \Delta \varepsilon^2 \rangle_{is} = \langle \Delta \varepsilon^2 \rangle_T + \langle \Delta \varepsilon^2 \rangle_\rho + \langle \Delta \varepsilon^2 \rangle_c \quad (5)$$

Scattering due to concentration fluctuations is related to the activity coefficients of the component  $\gamma_A$ ,  $\gamma_B$  (eq. 3), and investigation of the molecular nature of both concentration fluctuations and scattering are thus possible.

In the traditional approach fluctuations of internal variables, such as the extents  $\{\xi_\alpha\}$  (eq. 2), are not taken into account. Thus, eq. 5 is derived under the assumption that the external thermodynamic variables  $\{T, \rho, \text{ and } c\}$  determine uniquely the fluctuation state, and therefore it allows for fluctuations which do not disturb the equilibrium of the system with respect to internal processes.

Thermodynamic potentials for nonequilibrium states of the system, taking into account both scalar  $\{\xi_\alpha\}$  and tensorial  $\{\eta_{\beta,ik}\}$  internal variables have been constructed, and fluctuation theory was developed [4–8]. For fluctuations in nonequilibrium with respect to internal parameters ( $A \neq 0$ ), the formulae for extensive variables (energy, volume) coincide with those obtained for equilibrium ( $A = 0$ ) fluctuations,  $\langle \Delta E^2 \rangle = kT^2 C_V^o$ ,  $\langle \Delta V^2 \rangle = kTV\beta_T^o$  [20]. In contrast, fluctuations of intensive variable (temperature, pressure) are determined by the instantaneous ( $\xi = \text{const}$ ) values of the parameters,  $\langle \Delta T^2 \rangle = kT^2/C_V^\infty = \langle T^2 \rangle_A + kT^2(1/C_V^\infty - 1/C_V^o)$  where  $C_V^o$  and  $C_V^\infty$  are the equilibrium ( $A = 0$ ) and instantaneous ( $\xi = \text{const}$ ) isochoric heat capacity.

The contributions from fluctuations of extents to thermodynamic properties, e.g., the isobaric heat capacity  $C_p$  and the isothermal compressibility  $\beta_T$  or Rayleigh scattering have been established. In order to exhibit a scattering process, reagents must be different in enthalpy and polarizability. Thus, this may be a source of new data on the internal processes in matter.

The Rayleigh ratio for anisotropic scattering  $R_{an}$  is determined by the average molecular anisotropy  $R_{an} \sim \langle \gamma^2 \rangle = g^{opt} \gamma^2$ , where  $\gamma^2$  is the molecular anisotropy, and  $g^{opt}$  is the optical correlation factor. The relationships between optical factors, the structure of the aggregates and the thermodynamics of their formation have been revealed [4–8].

The dipole factors  $g^d$  (eq. 4) are determined by the mutual orientations of the dipole moments and the optical ones  $g^{opt}$  by those of the molecular polarizability. Thus, it allows complementary information on the structure of supramolecular species to be obtained and, moreover, it is possible to calculate the dielectric properties from the optical ones and vice versa.

Thus, these methods allow to obtaining new data on the thermodynamics of aggregation, structure and properties of aggregates, and integral and differential parameters of association, allowing us to study aggregates with long-range molecular correlations.

## QUASICHEMICAL MODELS IN INVESTIGATIONS OF RELAXATION PHENOMENA AND DYNAMIC PROCESSES IN LIQUIDS

The macroscopic description of irreversible processes is based on methods of nonequilibrium thermodynamics [1,16,20,21]. The local balance equations for extensive variables, in combination with the relations of fluxes of mass, momentum, energy, etc., to thermodynamic forces (gradients of velocity, concentration, temperature, etc.) form the set of equations used to describing the spatio-temporal evolution of nonequilibrium systems. Onsager's kinetic coefficients  $L_{\alpha\beta}$ , relating thermodynamic fluxes and forces, are determined by the rate constants, diffusion coefficient, and bulk and shear viscosity, etc. Those should either be determined from experiment or by using molecular theory.

Experimental methods are of considerable importance for investigations of dynamic processes, and the results are interpreted commonly by models [22,23]. Thermodynamic models of systems with internal parameters hold a prominent position among those. Models provide the interpretation of internal variables, for instance, the extents of quasicheical processes  $\{\xi_\alpha\}$  for conformation transitions and energy-transfer processes. Scalar, vectorial, or tensorial approaches are used for structural and dipole relaxation, etc.

Thus, the importance of the extended quasichemical models for studies of dynamical processes in liquids is clear. The first one is the theory of kinetic coefficients of nonequilibrium thermodynamics, the second one is the theory of relaxation (acoustic, dielectric) spectra, and the third one is the application to dynamic processes occurring in liquids. Extending to nonlinear irreversible phenomena seems promising. Molecular thermal motion is responsible for the local equilibrium in matter; this is the basic point for the thermodynamic approach to nonequilibrium phenomena. Molecular thermal motion in liquids presents the elementary steps also found in more complex systems such as chemical reactions.

Processes of molecular thermal motion contribute both to equilibrium properties of liquids, e.g., thermodynamic potentials and excess functions of the mixture (eq. 3), compressibility, heat capacity, static permittivity  $\epsilon_S$  (eq. 4), integral Rayleigh ratio  $R$  (eq. 5), and to kinetic and relaxation properties, e.g., the rate constants of chemical reactions and those of internal processes  $k_\alpha, k'_\alpha$  (eqs. 1,6), volume  $\eta_V$  (eq. 6), and shear  $\eta_s$  viscosity, diffusion coefficient  $D$ , dynamic compressibility  $\beta_S^*(\omega) = \beta_S'(\omega) + i\omega\eta_V(\omega)$  (eq. 6), permittivity  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ , and Rayleigh ratio  $R(\omega)$ , which depend on the frequency  $\omega$ . Thus the relationships of the thermodynamics and kinetics of the processes occurring in a matter are exhibited [4–8].

Considering the scalar variables  $\{\xi_\alpha\}$  and the present examples from acoustic spectroscopy: The complex adiabatic compressibility  $\beta_S(\omega)$ , defining the velocity  $V$  and the absorption  $\alpha$  of longitudinal acoustic waves, is given by the expression [25]:

$$\beta_S^*(\omega) = \beta_S'(\omega) + i\omega\eta_V(\omega) = \beta_S^\infty(\omega) + \sum_{\alpha=1}^r \frac{b_\alpha \beta_S^0}{1 + \omega^2 \tau_{pS,\alpha}^2} + i\omega \sum_{\alpha=1}^r \frac{b_\alpha \beta_S^0 \tau_{pS,\alpha}}{1 + \omega^2 \tau_{pS,\alpha}^2} \quad (6)$$

In eq. 6,  $b_\alpha = \delta_\alpha \beta_S / \beta_S^0 = (\beta_{S,\alpha}^0 - \beta_{S,\alpha}^\infty) / \beta_S^0$  are the relaxation strengths of normal reactions;  $\eta_V(\omega)$  is the dynamic bulk viscosity. The relaxation times of normal reactions  $\tau_{pS,\alpha}$  are determined by the eigenvalue problem  $\tau^{-1} \mathbf{x} = \mathbf{LHx}$ , where  $\mathbf{L}$  is the diagonal matrix and the elements of that are proportional to both the rate constants  $k_\alpha$  (or  $k'_\alpha$ ) for direct (or reverse) process  $\alpha$  (eq. 1) and the concentrations of the reagent according to the law of mass action. The elements of the matrix  $\mathbf{H}$  are the second derivatives of the enthalpy with respect to the extents of the natural reaction  $\{\xi\}$ . The eigenvectors  $\mathbf{x}_\alpha$  define a transformation matrix  $\xi = \mathbf{X}\zeta$  from the extents of the natural reaction  $\xi$  to those of the normal one  $\zeta$ . In order to observe the process in the acoustic spectrum it should possess nonzero enthalpy  $\Delta H_\alpha = (\partial H / \partial \xi_\alpha)_{T,P}$  or volume  $\Delta V_\alpha = (\partial V / \partial \xi_\alpha)_{T,P}$  variations.

In dielectric spectroscopy, the complex permittivity  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$  is investigated,  $\epsilon'(\omega)$  is the dynamic permittivity and  $\epsilon''(\omega)$  is the dielectric loss; it is represented similarly to eq. 6 [26]. In order to observe this process in a dielectric spectrum, it should result from a nonzero variation of the dipole moment of the system,  $(\partial M / \partial \xi_\alpha)_{T,P} = \Delta M_\alpha \neq 0$ .

The equations defining the relaxation times  $\tau_\alpha$  and relaxation's strengths  $b_\alpha$  (eq. 6) for nonideal solutions were derived. The applications yielded new data on the thermodynamics and kinetics of reorganization of the supramolecular ordering, conformational transitions of the molecules, and energy-transfer processes as well as on the spatio-temporal hierarchy of the processes of the molecular thermal motion [4–8]. Thus, the methods developed extend the quasichemical concept to the kinetic properties of liquid systems.

## APPLICATIONS FOR MIXTURES

Let us now characterize applications to binary solutions (see for the review [6–8]).

### Binary mixtures with negative deviation from ideal solution behavior

Propanone-trichloromethane and dimethylsulfoxide-trichloromethane mixtures were considered as systems with a negative deviation from ideality. The propanone-trichloromethane mixture was described

by model  $A + B + AB + AB_2$ , for dimethylsulfoxide-trichloromethane it was necessary to include the dimerization of dimethylsulfoxide ( $A + B + AB + AB_2 + A_2$ ). The models proposed describe the activity coefficients, excess Gibbs energy, enthalpy, and entropy as well as permittivity and Rayleigh ratios in the whole concentration range of the mixtures. The major contributions to the excess thermodynamic functions are generated by the specific interactions, and the role of the universal ones is reduced to partial compensation of the association contribution. Universal interactions lead to a dependence of the “concentration” equilibrium constants on the composition of the mixture, which is varied up to 30 %. This is essential if one wants to study the thermodynamics of aggregation. Mixtures with negative deviation from ideality are characterized by relatively small numbers of association, for instance in propanone-trichloromethane mixture the maximum number of association is  $n_{AB} = 1.25$  ( $T = 313$  K). Thus, the molecular correlations extend to no more than the first coordination shell.

### Binary mixtures with positive deviation from ideal solution behavior

Monohydric alcohol solutions demonstrate a generally positive deviation from ideality. We can distinguish at least four types of alcohol mixtures. The first ones are mixtures of nonpolar “inert” solvent-associating solutes, e.g., cyclohexane-cyclohexanol. The second ones are mixtures of nonpolar “solvating” solvent-associating solutes, e.g., tetrachloromethane-methanol. The third ones are mixtures of polar “solvating” solvent-associating solute, e.g., ketone-alcohol or trichloromethane-alcohol. The fourth ones are mixtures of associating solvent-associating solute, e.g., methanol-butanol or alcohol-*N*-amide.

Mixtures similar to cyclohexane-cyclohexanol were described by model  $A_1 + B_1 + B_2 + B_3 + \dots + B_k + \dots + B_{l,cycl}$ . The mixtures of the second and third type were treated by model  $A_1 + B_1 + B_2 + B_3 + \dots + B_k + \dots + B_{l,cycl} + AB_1 + AB_2 + AB_3 + \dots + AB_m + \dots$ . For mixtures of the fourth type the more general model  $A_1 + B_1 + B_{l,cycl} + A_m B_n$  ( $m, n \geq 1$ ) was applied. It was found from Monte Carlo simulations of methanol in a cell containing 500 molecules [25] that the most probable cyclic aggregate consists of four molecules [7,8].

The numbers of association are very high in methanol  $\bar{n}_B \cong 60$ ,  $T = 298$  K and decrease dramatically upon dilution. It has been found here to be much larger than in Monte Carlo simulations ( $\bar{n}_B \cong 12$ ), probably due to an insufficient simulation box size [7,8,25]. Cyclic aggregates are important only in mixtures poor in alcohol, according to the higher stability of nonpolar aggregates in a less polar medium. In pure alcohol chain-like aggregates are the dominating ones,  $w_{cycl} \cong 2$  %. It has been concluded that models of alcohol mixtures taking into account only one or a few types of aggregates are not adequate [4–8].

In general, the models developed give a good description of thermodynamic functions, permittivity, and light scattering of alcohol solutions. The contributions by universal interactions to the excess thermodynamic functions of alcohol mixtures are comparable with the ones originating in association and do not reduce to their partial counterbalancing as is the case for propanone-trichloromethane mixture. Therefore, again, the universal contributions are necessary for a proper study of association. Dipole  $g_s^d$  and optic  $g_s^{opt}$  factors are much more sensitive to aggregate structures in comparison with the permittivity  $\epsilon_s$  and the anisotropic ratio  $R_{an}$ . The Rayleigh concentration ratio contributes up to ~70–80 % of scattering in alcohol mixture, in contrast, anisotropic scattering is about 1–2 orders less.

### CONCLUSION

The methods developed allow to obtaining new data on the thermodynamics and kinetics of the internal processes in mixtures, especially on the supramolecular organization. Firstly, they allow us to analyze the different physicochemical properties of the wide class of mixture in a wide range of the parameters on the unified molecular approach. The results obtained allow us to extend this approach to



multicomponent mixtures, and thus properties of ternary mixtures can be predicted from the data obtained for binary ones.

Secondly, they allow us to investigate the composition, structure, dipole moment, and polarizability of the aggregates in mixtures as well as their thermodynamics and kinetics of aggregation, including both differential and integral characteristics. The models developed take into account the cooperativity of H-bonding. Thus, a detailed description of the supramolecular organization of mixtures can be obtained. Data on the long-range molecular correlations are difficult or impossible to obtain by other methods, e.g., spectroscopy or diffraction. The data obtained on the thermodynamics of aggregation (Gibbs energy, enthalpy, and entropy of aggregation, extracted from the respective equilibrium constants) are collected and tabulated in [7,26].

Thirdly, the models developed describe the properties of mixture in the whole concentration range, and thus include pure solvents, diluted and concentrated solutions. They enable both a description and prediction of properties over a wide temperature range.

Fourthly, the equations derived define the thermodynamic potentials of the nonequilibrium states and the fluctuations of the internal variables with their contributions to macroscopic properties. They thus extend the quasichemical concept for kinetic and relaxation properties of nonideal mixtures.

Supramolecular ordering leads to manifold consequences for the properties of mixture. Different types of supramolecular organization characterize mixtures with negative and positive deviations from ideal behavior. In mixtures with a negative deviation from ideality, the main role belongs to complexation of dissimilar molecules, and, in contrast in mixtures with a positive one, the association of homogeneous molecules usually plays the main role. Thermodynamic properties are sensitive to the stoichiometry of the aggregation and not to the structure of aggregates. Both dielectric and optical properties are related to the spatial ordering of molecules. Therefore, joint application of the methods developed to different properties of mixtures allows us to obtain complementary information on the structure of aggregates, which is not possible with other methods, especially when long-range molecular correlations are present.

Self-organization in mixtures by attractive directed molecular interactions like H-bonds leads to supramolecular aggregates consisting of tens of molecule. The supramolecular aggregates of nanosizes play an important role for a new understanding of the role of long-range molecular correlations for the structure and properties of liquids.

The basis of a unified approach, relying on the concept of supramolecular assemblies and including thermodynamic, dielectric, optic, and kinetic properties of liquids has been elaborated. The results presented contribute to the background of supramolecular thermodynamics and kinetics for the analysis of the properties of liquids, defined by different molecular parameters, and studying the long-range molecular correlations and aggregates up to nanosizes. Studying supramolecular ordering in mixtures contributes to a molecular understanding of supramolecular chemistry and self-organization phenomena in disordered condensed matter, leading to the possibility of predicting macroscopic properties. The molecular design of liquid materials can be envisaged. These models, developed for describing microscopic stages of supramolecular ordering in molecular liquids, reflect the general features of the self-organization phenomena in more complex systems with larger spatio-temporal scales.

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