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MOLECULAR MODELLING OF THERMODYNAMIC AND RELATED PROPERTIES OF MIXTURES

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Abstract

The results of recent developments on modelling of supramolecular ordering and physicochemical properties of molecular mixtures have been reviewed. The main attention is paid to the unified approach based on a generalised quasichemical model for a set of thermodynamic, dielectric and optical properties of mixtures, self-organized by specific bonding. Interrelations between thermodynamic, as well as dielectric, and optical properties of liquid mixtures, reflecting different molecular parameters, and the characteristics of quasichemical processes are presented. Applications for thermodynamic functions of mixing, permittivity, coefficients Rayleigh light scattering in molecular mixtures are considered. Data on thermodynamics of aggregation in mixtures have been obtained.

Keywords: modelling of supramolecular ordering of molecular mixtures, physicochemical properties of molecular mixtures

Introduction

The development of the theory of liquids is based upon fundamental investigations of their structure, the nature of molecular interactions, and dynamic processes proceeding during the thermal motion of molecules. The increasing role of investigations of liquids by combining the methods, as well as the problem of design of liquid materials on the molecular-structural level, require approaches for analyzing and predicting a set of macroscopic properties on the basis of a general concept. Model approaches are applied mainly to complex molecular liquids. Among these the lattice model for thermodynamic properties of molecular mixture, based on Guggenheim–Barker theory and its further modifications, and especially the quasichemical model for self-organised specific bonding liquids must be mentioned [1–4].

In the framework of the quasichemical concept the processes are represented by the equations of chemical reaction:

$$\sum_{i} \nu_{i\alpha} M_{i} \underset{k'_{\alpha}}{\overset{k_{\alpha}}{\rightleftarrows}} \sum_{i} \nu'_{i\alpha} M'_{i} \quad (\alpha = 1,2,\ldots,r) \tag{1}$$

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

where M_i designates the type of the i-th reagent, $\nu_{i\alpha}$ and $\nu'_{i\alpha}$ denotes the stoichiometric coefficients of one in the reaction α, ξ_α, and A_α denotes the degree of advancement (or extent), and the thermodynamic affinity of the quasichemical process α respectively, and μ_i here is the chemical potential of the i-th reagent.

Quasichemical models combine both macroscopic and molecular-statistical theory. Really one can treat this approach as an extension of chemical thermodynamic and kinetic methods to internal processes occurring in matter; such as reorganizations of intermolecular structure, and in particular, the association processes, the processes of energy transfer between molecular degrees of freedom, conformation transitions of molecules, and related fluctuation phenomena. Molecular-statistical models are used to specify the nature of processes described by Eq. (1), and to derive equations for physicochemical properties [3, 4].

The quasichemical method has usually been applied to thermodynamic and spectroscopic properties of liquids [1, 2, 5]. Recently, along with the elaboration of thermodynamics of association models [6, 7], this approach has been extended to dielectric [8–10], optical [3, 11], and kinetic [12] properties of molecular mixtures. The object of this present article is to characterise some of these results and its applications.

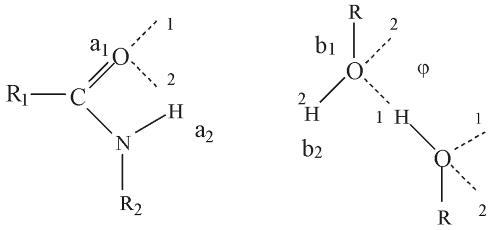
Characteristics of quasichemical models

We have to decide on the next interrelated problems for describing supramolecular ordering and properties of liquids in the quasichemical approach. Firstly we have to describe the structure, composition, electrical, optical properties of the supramolecular species. Secondly we have to develop the thermodynamics of these and thirdly we have to derive the equations for macroscopic thermodynamic, electrical, optical, kinetic properties of mixtures.

The topological features of the supramolecular form, the most typical of them – linear, cyclic, branched star-, comb, tree-like, and net-like must be taken into account. Mainly the number of specific bonds formed by molecules determines these features. If the number of bonds is not greater than two, chain or cyclic associated species are possible, e.g., monohydric alcohols and phenols, monobasic acids, *N*-amides, amines, hydrogen halides. If the molecule is involved in three or more specific bonds (e.g. water, polyhydric alcohols, polybasic acids, etc.) branched and spatial networks structures can be formed [3, 4, 12].

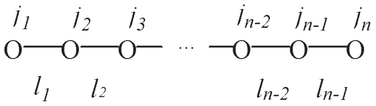
The models of one component homogeneous association (models A_1+B_1+B_n, and A_1+B_1+B_2+...+B_n+...), and models with complexation of components (models A_1+B_1+A_1B_1 and A_1+B_1+A_1B_1+A_1B_2), were mainly considered [1, 2, 5]. This author examined for the first time a mixture of associated species of arbitrary composition.

Consider a binary solution of components *A* and *B* and suppose molecules *a* and *b* contain groups of atoms a_1, a_2 and b_1, b_2 respectively. These groups take part in the following bonding: $a_1 \ldots a_2 = aa$, $a_2 \ldots b_1 = ab$, $b_2 \ldots a_1 = ba$, and $b_1 \ldots b_2 = bb$. Thus for an *N*-monosubstituted amide – monohydric alcohol mixture these bonds are *CO...HN* (*aa*), *NH...OH* (*ab*), *OH...OC* (*ba*), *OH...OH* (*bb*) (3):



(3)

In general each pair of molecules can form a specific bond, e.g. *OH...OH,* in one of the several ways which differ in the spatial disposition of the molecules. Thus the oxygen atom of alcohol has two lone pair of electrons and the *OH...OH* bond can be either of type ‘1’ or ‘2’; a similar situation occurs also with *N*-amides (3). I refer to ways of bonding as the states of bond and denote them by the index l_i. One can assume the number of the states of bond $q_{j_1 j_2}$ (j_1, $j_2 = a, b$) are equal, therefore $q_{aa} = q_{ab} = q_{ba} = q_{bb} = q$. Thus, the associated species comprising *n* molecules is described by the sets of subscript $\{n, j_1, j_2, \ldots j_n, l_1, l_2, \ldots l_{n-1}\} \equiv n, \{j_k\}, \{l_i\}$, where the index $j_k = a,b$ ($k = 1, 2, \ldots n$) indicates the type of the *k*-th molecule, and the index $l_i = 1, 2, \ldots, q$ ($i = 1, 2, \ldots n-1$) denotes the state of the *i*-th bond in it:



(4)

Thus, we consider associated species of arbitrary composition with different ways of bonding. In particular allowance for the latter factor leads to the structural polyvariability of the associates. Actually starting from the first ‘root’ molecule various ways for further growth of the associated species are possible. Thus, we obtain the variety of supramolecular structures. The properties of these associates, e.g., structure, dipole moment, polarizability tensor, etc., differ, as do the macroscopic properties of the respective liquid systems. Altogether, this required the development of approaches for describing microscopic properties of supramolecular species and corresponding ones for macroscopic properties of mixtures.

Thermodynamics of associated species mixtures

Prigogine–Defay equations [5] $\mu_A = \mu_a$, $\mu_B = \mu_b$, relating the chemical potentials of solution components μ_A and μ_B, and those of monomer molecules μ_a and μ_b, are the starting point for determining interrelations of thermodynamic properties of solution and microscopic properties of supramolecular species. In a symmetrical reference system [5, 13] these equations leads to the following expressions for the activity coefficients of component γ_A, γ_B:

$$\gamma_A = \frac{\gamma_a x_a}{\bar{\gamma}_a \bar{x}_a x_A^0}, \quad \gamma_B = \frac{\gamma_b x_b}{\bar{\gamma}_b \bar{x}_b x_B^0} \tag{5}$$

where x denotes the mole fraction, γ_a, γ_b denote the activity coefficients of the monomer molecule; bar henceforth used for the quantity referring to the pure component. The specific form of Eq. (5) is determined by both the types of associative equilibria and the theoretical model applied for the mixture of associate. The expressions for the excess thermodynamic functions, such as Gibbs energy G^E, enthalpy of mixing H^E can be derived from Eq. (5) by the standard procedure [5, 13].

The hierarchy of theoretical models of an associated species mixture is defined by the description of universal interactions, determining the deviations from ideal solution, has been reviewed in [3, 4]. A model approach for molecular interaction contributions to thermodynamic functions (Gibbs energy, enthalpy, and entropy) of mixtures was developed [6, 7, 12, 14]. Repulsive interactions are treated within the framework of the Flory approach, dipole interactions are described using a self-consistent Onsager's reaction field model, dispersion interactions are taken into account by a one-centre continuous approach, and specific cases are dealt with by the association model. Thus the activity coefficients γ_A, γ_B (Eq. (5)) and excess thermodynamic functions (e.g. enthalpy of mixing H^E) include three contributions, corresponding first, associative, second, dispersion and third, dipole forces:

$$\gamma_{A(B)} = \gamma_{A(B)}^{ass} \gamma_{A(B)}^{dis} \gamma_{A(B)}^{dip}, \quad H^E = H^{E,\,ass} + H^{E,\,dis} H^{E,\,dip} \tag{6}$$

The first terms in Eq. (6) describe deviations from ideal solution due to the repulsion and specific attraction interactions:

$$\gamma_{A(B)}^{ass} = \frac{C_{a,b}}{\bar{C}_{a,b} x_{A,B}^0} \exp\left(\frac{1}{\bar{n}_{A,B}} - \frac{\varphi_{A,B}^0}{x_{A,B}^0 n_{AB}} \right) \tag{7}$$

In Eq. (7) $C_{a,b}$ are the molar concentrations of the monomer molecules a and b, $x_{A,B}^0$ and $\varphi_{A,B}^0$ are the stoichiometric mole and volume fractions of the component, $\bar{n}_A$, $\bar{n}_B$ are the average number of association in individual liquids A and B, and n_{AB} is an average number of association in solution, determining the mean number of molecules in aggregates:

$$n_{AB} = (C_A^0 + C_B^0) / \sum_{n,\{j_k\}\{l_i\}} C_{n,\{j_k\}\{l_i\}} \tag{8}$$

where C_A^0, C_B^0 are the stoichiometric molar concentrations of the component.

The formation of aggregates is described by the equilibrium dimerization constants $\{K_{j_1 j_2 l_i}\}$ and, for formation of the higher-order ($n \geq 3$) associated species $\{K'_{j_1 j_2 l_i l_2}\}$. The molar concentrations of associated species are given by the formulas:

$$C_{\mathrm{n}\{\mathrm{j_k}\},\{\mathrm{l_i}\}} = C_{\mathrm{j_1}} K_{\mathrm{j_1 j_2},\mathrm{l}_i} C_{\mathrm{j_2}} \prod_{\mathrm{m}=2}^{\mathrm{n}-1} (K'_{\mathrm{j_m j_{m+1}},\mathrm{l_{m-1}},\mathrm{l_m}} C_{\mathrm{j_m}}) \tag{9}$$

The total concentration of associated species and monomer molecules is given by Eq. (10) derived by the matrix technique [3, 8, 14]:

$$C = \sum_{\mathrm{n}\ge 1} \sum_{\{\mathrm{j_k}\}} \sum_{\{\mathrm{l_i}\}} C_{\mathrm{n}}\{j_{\mathrm{k}}\}\{l_{\mathrm{i}}\} = C_{\mathrm{a}} + C_{\mathrm{b}} + \widetilde{C} V (E_{2\mathrm{q}} - V')^{-1} I_{2\mathrm{q}} \tag{10}$$

where $\widetilde{C}=[C_{\mathrm{a}}\ C_{\mathrm{b}}]$, $\boldsymbol{E}_{2\mathrm{q}}$ is the unit matrix, and $\boldsymbol{I}_q$ is the vector consisting of units, and

$$V = \begin{bmatrix} V_{\mathrm{aa}} & V_{\mathrm{ab}} \\ V_{\mathrm{ba}} & V_{\mathrm{bb}} \end{bmatrix}, (V_{\mathrm{j_1 j_2}})_{\mathrm{l_1}} = K_{\mathrm{j_1 j_2},\mathrm{l_1}} C_{\mathrm{j_2}},\ V' = \begin{bmatrix} V'_{\mathrm{aa}} & V'_{\mathrm{ab}} \\ V'_{\mathrm{ba}} & V'_{\mathrm{bb}} \end{bmatrix}, (V'_{\mathrm{j_1 j_2}})_{\mathrm{l_1 l_2}} = K'_{\mathrm{j_1 j_2},\mathrm{l_1 l_2}} C_{\mathrm{j_2}} \tag{11}$$

The mean number of association n_{AB} (Eq. (8)) is expressed as follows:

$$n_{\mathrm{AB}} = \frac{C_{\mathrm{A}}^{0} + C_{\mathrm{B}}^{0}}{C} = \frac{C_{\mathrm{a}} + C_{\mathrm{b}} + \widetilde{C} V (2E_{2\mathrm{q}} - V')(E_{2\mathrm{q}} - V')^{-2} I_{2\mathrm{q}}}{C_{\mathrm{a}} + C_{\mathrm{b}} + \widetilde{C} V (E_{2\mathrm{q}} - V')^{-1} I_{2\mathrm{q}}} \tag{12}$$

In Eqs (10) and (12) the stoichiometry of the aggregation is included in the matrices $\boldsymbol{V}$, $\boldsymbol{V}'$ (Eq. (11)). Thus, if in the matrices $\boldsymbol{V}$, $\boldsymbol{V}'$ only $\boldsymbol{V}_{\mathrm{bb}}$, $\boldsymbol{V}'_{\mathrm{bb}}$ are the non-zero blocks, it corresponds to the solution of an associating substance B in an inert solvent A, model $A_1+B_1+B_2+\ldots+B_{\mathrm{n}}+\ldots$. If as $\boldsymbol{V}_{\mathrm{ba}}$, $\boldsymbol{V}'_{\mathrm{ba}} \neq 0$, as $\boldsymbol{V}_{\mathrm{bb}}$, $\boldsymbol{V}'_{\mathrm{bb}} \neq 0$, it relates to the solution of an associating substance B in a solvating solvent A, model $A_1+B_1+B_2+\ldots+B_{\mathrm{n}}+\ldots+A_1B_1+A_1B_2+\ldots+A_1B_{\mathrm{m}}+\ldots$, etc.

The multipliers $\gamma_{\mathrm{A,B}}^{\mathrm{dis}}$ and $\gamma_{\mathrm{A,B}}^{\mathrm{dip}}$ in Eq. (6) describe the contribution of dispersion and dipole interactions to the non-ideality of a solution respectively; corresponding expressions for those have been given in works [3, 4, 6, 7]. The approach developed relates the thermodynamic non-ideality to molecular properties. The molecular force contributions to Gibbs energy, enthalpy, and entropy of pure liquids have been calculated. For moderately polar substances such as monohydric alcohols the major contributions come from the dispersion interaction and H-bonding, whereas the longe-range constituents of dipole force is of only minor importance. As to the strongly polar *N*-amides the three contributions mentioned are comparable. The heat of evaporation of polar associated liquids is reproduced quite well [3, 4].

The multivariance of the associated species as far as both the composition and structure is concerned results in different types of dependence of mixing functions on solution composition. For the formation of homogeneous associates the influence on thermodynamic functions is essential if there is a difference in the stoichiometry of association, e.g., dimerization B_1+B_2 and the continuous association $B_1+B_2+\ldots+B_{\mathrm{n}}+\ldots$. Thus models with the same stoichiometry and different associate structure, e.g., linear and cyclic dimers cannot be discriminated by thermodynamic study. Corresponding information cannot be obtained either by IR and NMR spectroscopy techniques, as well by diffraction methods.

Thus progress in the study of long-range supramolecular ordering in mixtures has proved to be possible on the basis of an approach for the permittivity and Rayleigh light scattering.

Quasichemical models in the dielectrometry of mixtures

The application of dielectric constant data to study supramolecular organisation of liquids is based first on models of mixtures of associated species, and second on the theory of dielectric properties. The following equation was obtained for the permittivity of a mixture ε_s on the basis of fundamental equation given by Frohlich [15] by the semi-microscopic method for separating the orientational and deformational polarisation's [9]:

$$\frac{9k_B T V_m}{4\pi N_0 \varepsilon_s}\sum_{j=1}^{k}\left(\frac{\varepsilon_s-\varepsilon_{\infty j}}{2\varepsilon_s+\varepsilon_{\infty j}}\right)\varphi_j^0=\sum_{j=1}^{k}\left(\frac{\varepsilon_{\infty j}+2}{2\varepsilon_s+\varepsilon_{\infty j}}\right)^2 x_j^0\mu_j^0 g_j^d \tag{13}$$

where μ_j is the dipole moment of a molecule and μ_j^* is of a sphere in the dielectric with a fixed one molecule in it, $g_j^d=<\mu_j\mu_j^*>/\mu_j^2$ (j=1,2,...k) is the dipole correlation factor of the j-th component. The dipole factor of the solution g_s^d is given by the formula:

$$g_s^d=\frac{9k_B T}{4\pi N_0\varepsilon_s}\frac{\sum_{j=1}^{k}x_j^0 V_{m,j}[(\varepsilon_s-\varepsilon_\infty)/(2\varepsilon_s+\varepsilon_{\infty,j})]}{\sum_{j=1}^{k}x_j^0\mu_j^2[(\varepsilon_{\infty,j}+2)/(2\varepsilon_s+\varepsilon_{\infty,j})]^2}=\frac{\sum_{j=1}^{k}g_j x_j^0\mu_j^2[(\varepsilon_{\infty,j}+2)/(2\varepsilon_s+\varepsilon_{\infty,j})]^2}{\sum_{j=1}^{k}x_j^0\mu_j^2[(\varepsilon_{\infty,j}+2)/(2\varepsilon_s+\varepsilon_{\infty,j})]^2} \tag{14}$$

The deviation of dipole factors of g_s^d, g_j^d (Eqs (13) and (14)) from unity is due to the correlations of molecular dipole moments. Equations relating the dipole factors to the structure of a supramolecular species and the thermodynamic parameters of their formation were obtained in [8].

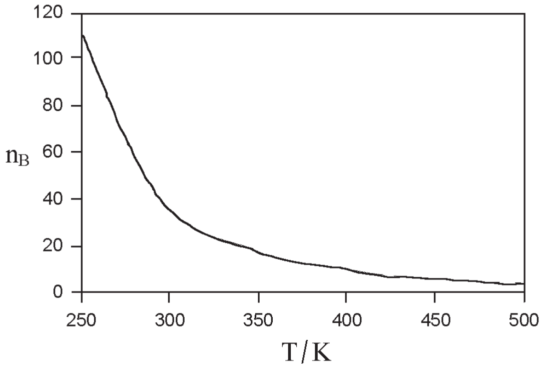


Fig. 1 Temperature variation of the average number of association of methanol (ΔT=253÷493 K)

The relationships derived allow quite detailed data to be obtained on the composition, structure and thermodynamics of aggregation, inaccessible by other methods particularly as regards long-range molecular correlations. Models with the same stoichiometry of associates and different structures to those (e.g., chain-like and cyclic) may be distinguished, even qualitatively. The applications to monohydric acyclic, alicyclic, and aromatic alcohols, and *N*-amides was demonstrated; there is the possibility of a fairly reliable discrimination of the models [3, 4]. The association constants, the enthalpy ΔH and enthalpy ΔS of H-bonding (Tables 1, 2) were found. These models both enable a description of permittivity over a wide temperature range.

Table 1 Enthalpy ΔH (kJ mol^{-1}) and entropy ΔS (J mol^{-1} K^{-1}) of the association in *n*-alkanols

Alcohol	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH	$C_5H_{11}OH$	$C_6H_{13}OH$	$C_7H_{15}OH$
$-\Delta H$	19	19	20	20	19	19	19
$-\Delta S$	48	52	69	62	57	57	60
$-\Delta H'$	21	22	22	21	22	22	22
$-\Delta S'$	46	50	58	59	59	59	66

Table 2 Enthalpy ΔH (kJ mol^{-1}) and entropy ΔS (J mol^{-1} K^{-1}) of the association for the alicyclic and aromatic alcohols

Alcohol	$-\Delta H$	$-\Delta S$
Cyclohexanol	26	72
4-Methylcyclohexanol	23	65
1-Cyclohexylpropanol-1	13	46
Phenylmethanol	20	64
2-Phenylethanol	21	65
1-Phenylethanol	18	56
Phenyl-*t*-buthanol	16 (*l*) 15 (*c*)	49 (*l*) 58 (*c*)

Especially the long-range correlations by H-bonding must be underlined. Thus the mean number of association $\overline{n}$ in pure alkanols is equal to ten and above at room temperature and increases with decreasing temperature (Fig. 1). Analysis of the size distribution of methanol aggregates shows that in pure methanol at T=293 K the fraction of aggregates containing more than 40 molecules is 38%, and the fraction of those consisting of more than 80 molecules equals 14% [4].

Quasichemical models in Rayleigh light scattering

Rayleigh light scattering can be subdivided to isotropic scattering and anisotropic one [16]. Isotropic fluctuation of permittivity (refractive index, $\varepsilon=n^2$), and Rayleigh coefficient are usually expressed as a sum of the terms, interpreted as due to independent fluctuations of temperature, density, and concentration:

$$R_{\mathrm{is}} \approx \left\langle \Delta\varepsilon^2 \right\rangle_{\mathrm{is}} = \left\langle \Delta\varepsilon^2 \right\rangle_{\mathrm{T}} + \left\langle \Delta\varepsilon^2 \right\rangle_{\mathrm{p}} + \left\langle \Delta\varepsilon^2 \right\rangle_{\mathrm{x}} \tag{15}$$

It must be mentioned firstly that the usual consideration of the terms in Eq. (15) reflecting independent fluctuations is incorrect because of the density-concentration fluctuation correlation. In reality the last two terms in Eq. (15) are determined as a result of correlated fluctuations of those. Secondly the traditional approach fluctuations of internal variables such as the extent of the quasichemical process $\{\xi_\alpha\}$ [Eq. (2)] are not taken into account [3, 12, 17].

Isotropic light scattering due to concentration fluctuations $R_{\mathrm{is,\,conc}}$ is related to the activity coefficients γ_{A} and γ_{B} by the Einstein–Smoluchovsky equation. Thus investigation of the nature of the concentration fluctuations is possible. The estimation of the contribution of fluctuations of the quasichemical process $\{\xi_\alpha\}$ to thermodynamic functions and to isotropic scattering was discussed in works [3, 4, 12].

The Rayleigh ratio for anisotropic scattering R_{an} is determined by the average molecular anisotropy $<\gamma^2>$ [3, 16]:

$$R_{\mathrm{an}} \sim \left\langle \gamma^2 \right\rangle = g^{\mathrm{opt}} \gamma^2, \;\; R_{\mathrm{an,\,s}} \sim \left\langle \gamma^2 \right\rangle = \sum_{\mathrm{j}=1}^{\mathrm{k}} \xi_{\mathrm{j}}^{0} \gamma_{\mathrm{j}}^{\mathrm{opt}} \gamma_{\mathrm{j}}^{2}, \;\; \gamma_{\mathrm{j}}^{\mathrm{opt}} = \left\langle \gamma_{\mathrm{j}} \gamma_{\mathrm{j}} \right\rangle / \gamma_{\mathrm{j}}^{2} \tag{16}$$

where γ^2 is the molecular anisotropy, g^{opt}, $g_{\mathrm{j}}^{\mathrm{opt}}$ are the optical correlation factors in liquid and in mixture, which are determined by the correlation of the axes of the molecular polarizability tensor. Equations relating the optical factors to the structure of a supramolecular species and the thermodynamic parameters of their formation were obtained in the studies [3, 12].

The dipole factors $g_{\mathrm{j}}^{\mathrm{d}}$ (Eqs (13) and (14)) are determined by the mutual orientations of dipole moments, and the optical factors $g_{\mathrm{j}}^{\mathrm{opt}}$ (Eq. (16)) by those of molecular polarizability. Thus joint application of these methods allows complementary information on the structure of supramolecular species to be obtained. Since both correlation factors are defined as concentration of associates as by the orientational potential of the molecule there is a possibility of calculating dielectric properties *a priori* from optical ones and *vice versa*. Thus for methanol involving complex association the experimental value of $<\gamma^2>$(exp.)=(0.31±0.04) 10^{-48} cm^6 and the calculated value of $<\gamma^2>$(cal.)=0.34 10^{-48} cm^6 coincide [18].

Applications for binary mixtures

We will characterise some applications to the study of supramolecular ordering in binary solutions, which rely on the analysis of the thermodynamic, dielectric and optic properties.

First we considered mixtures with weak structural ordering formed by non-polar and polar molecules, e.g. benzene, tetrachloromethane, cyclohexane, trichloromethane, dichloromethane [20], as regards both the comparison with strongly ordered systems and probing the methods for molecular interaction contributions to thermodynamic properties of the mixture. The approach satisfactorily describes the excess Gibbs energy G^E, enthalpy H^E, and entropy S^E; the greatest contributions to the excess function are made by the dipole interactions.

The binary mixtures essentially with supramolecular ordering can be divided according to thermodynamic properties of those with either negative or positive deviation from ideal solution [5, 13]. For these systems, on the basis of general results, the specific equations for thermodynamic functions of mixing, permittivity, and coefficients of light scattering were derived. The properties of the mixture are considered over as wide a concentration and temperature range as possible to incorporate the experimental data.

Binary mixtures with the negative deviation from ideal solution

The mixture acetone–chloroform [19] and dimethylsulfoxide–chloroform [20] were considered as systems with a negative deviation from ideality. The aggregation processes in acetone–chloroform mixtures were described by the model $A+B+AB+AB_2$, and for acetone–dimethylsulfoxide mixtures it as found necessary also to include dimerisation of dimethylsulfoxide (model $A+B+AB+AB_2+A_2$) where symbol A means acetone or dimethylsulfoxide and B denotes chloroform. The parameters of the model were the constants of complex formation, K_1, K_2, corresponding to the equilibria $A+B\Leftrightarrow AB$ and $AB+B\Leftrightarrow AB_2$, and also the constant K_3 for the dimerisation of dimethylsulfoxide.

The activity coefficients γ_A, γ_B, thermodynamic functions G^E, H^E, S^E, permittivity ε_s and Rayleigh ratios $R_{90,is}$ and $R_{90,an}$ in the temperature interval ΔT=288–328 K of the acetone–chloroform mixture have been analysed [19]. The constants K_1 and K_2 were calculated by solving the inverse problem for excess Gibbs energy G^E. From the equilibrium constants K_1 and K_2 the enthalpies of complex formation $\Delta H_1\cong \Delta H_2=-9\pm1$ kJ mol^{-1}, and the entropies $\Delta S_1=-25\pm5$ J mol^{-1} K, $\Delta S_2=-38\pm5$ J mol^{-1} K^{-1} were found. The excess enthalpy H^E, entropy S^E, permittivity ε_s, and Rayleigh ratios for the concentration $R_{90,conc}$ and anisotropic $R_{90,an}$ scattering were calculated without additional adjustment of the parameters.

The model explains a significant negative deviation thermodynamic functions G^E, H^E, S^E, from ideality. The major contributions to the activity coefficients and the excess functions are made by the specific interactions. For the activity coefficients and excess Gibbs energy the role of the universal interaction is reduced to partial compensation of the association contribution. Universal interactions lead to the dependence of the 'concentration' equilibrium constants on the mixture composition, which is varied up to 30%, and to the essential variations of the concentration of complexes in comparison with the commonly applied IAS model [1, 2, 5]. The dipole contribution to the excess enthalpy and entropy are larger but do not play the leading role either. The model gives fairly good reproduction of the permittivity and dipole factor. The dipole factor larger, than unity, demonstrates the tendency towards parallel alignment of the molecular dipoles in complexes AB and AB_2, and predicts small negative deviations (within 15–20%) from the linear dependence the Rayleigh ratio for anisotropic scattering. As to concentration scattering its intensity is very weak as a result of the large negative deviation from ideality in this mixture.

In general the proposed models describe the thermodynamic functions of mixing, as well as permittivity, and coefficient of light scattering in the whole range of concentration of the mixtures and over a wide temperature interval. The results obtained display a weak manifestation of supramolecular ordering in dielectric constant and anisotropic scattering due to both a small degree of association ($n_{AB} \leq 1.3$) and the structure of complexes in the acetone–chloroform and dimethylsulfoxide–chloroform mixtures with negative deviation from ideality. Thus the molecular correlation extends to no more than one or two co-ordination shells.

Binary mixtures with positive deviation from ideal solution

The second type of binary mixtures that demonstrate generally positive deviation from ideality comprises alcohol solutions. We can recognise at least three types of mixtures of monohydric alcohol [3]. First, solutions of alcohol in non-polar 'inert' solvents like cyclohexane–cyclohexanol [21]. Second solutions of alcohol in non-polar 'solvating' solvent, e.g. tetrachloromethane–methanol [22]. Third solutions of alcohol in polar 'solvating' solvent, e.g. cyclohexanone–cyclohexanol [23] and cyclohexanone–methylcyclohexanol [24].

Association in the mixture cyclohexane-cyclohexanol was described by the model $A_1+B_1+B_2+B_3+...+B_n+...$, hereinafter A denotes the molecule of the solvent, and B alcohol. The systems of the second and third type were treated using the model $A_1+B_1+B_2+B_3+...+B_n+AB_1+AB_2+AB_3+...+AB_m+ ....$

The parameters of the model were the equilibrium constants of the association of alcohol K and K', corresponding to the reactions $B+B \Leftrightarrow B_2$ and $B_n+B \Leftrightarrow B_{n+1}$, $n \geq 2$ for the chain-like association of alcohol, and the constant for the complex formation (solvation) of monomers and aggregates of alcohol with the solvent K_s, reaction $A+B_n \Leftrightarrow AB_n$, and the structural parameters of associates.

The constants of alcohol association K and K', as well as the structural parameters were determined by analysis of permittivity of pure alcohols [25, 26]. If there were no solvation, as in the case of the cyclohexane–cyclohexanol mixture, these parameters in principle are sufficient to describe other properties over the wide concentration and temperature ranges. The solvation constant K_s was estimated using a fitting procedure for the excess Gibbs energy of tetrachloromethane–methanol mixture, or for the dipole factor in the mixture ketone–alcohol. The excess enthalpy and entropy, the permittivity, and Rayleigh ratios $R_{90,\mathrm{conc}}$, $R_{90,\mathrm{an}}$ were calculated without additional adjustment of parameters.

The permittivity of the cyclohexane–cyclohexanol mixture was considered at ΔT=298–423 K, activity coefficients and excess functions at ΔT=298–328 K [21]. The enthalpies and entropies of H-bonding of alcohol were found $\Delta H=\Delta H'=-28\pm2$ kJ mol^{-1}, $\Delta S=\Delta S'=-76\pm4$ J mol^{-1} K^{-1}. The positive deviation from ideality in this mixture is explained by the association of alcohol, as well as to less extent by dipole interactions. Chain-like association determines the dipole factor above unity. Neglecting weakly polar aggregates of cyclohexanol probably causes overestimated values of the dipole factor in the region of low alcohol content.

Permittivity of the tetrachloromethane–methanol mixture was considered at ΔT=278–328 K, activity coefficients and excess functions at ΔT=293–353 K, and Rayleigh ratio at T=293 K [22]. The enthalpies of association of methanol are equal, $\Delta H \approx \Delta H' = -20\pm3$ kJ mol^{-1}; and its solvation by the tetrachloromethane ΔH_s= -16 ± 3 kJ mol^{-1}; the corresponding entropies are $\Delta S \approx \Delta S' = -20\pm5$ J mol^{-1} K^{-1}, ΔS_s= -24 ± 5 J mol^{-1} K^{-1}.

The contribution from dipole interaction to excess Gibbs energy and enthalpy are comparable with the association contribution and do not reduce to a partial counterbalancing as was the case for the acetone–chloroform mixture. The theoretical curve for permittivity do not give a very good fit with the correlation factor for the region of low concentration of methanol and the reason may lie in the neglect of the weakly polar cyclic aggregates. This disagreement reduces substantially in the case of permittivity. There exist great concentration fluctuations in the tetrachloro–ethane–methanol mixture, and thus the concentration light scattering in it measures 70–80% of the entire scattering. The Rayleigh ratio for concentration scattering fits the experimental data fairly well. The intensity of anisotropic scattering is about 1–2 orders less and is defined with poor accuracy. There are no satisfactory data available on anisotropic scattering for the whole composition range. However for pure methanol the model predicts the mean molecular anisotropy in good agreement with experimental data [18].

The mean numbers of association tetrachloromethane–methanol mixture at T=293 K are presented in Fig. 2. The number of association n_{AB} decreases upon dilu-

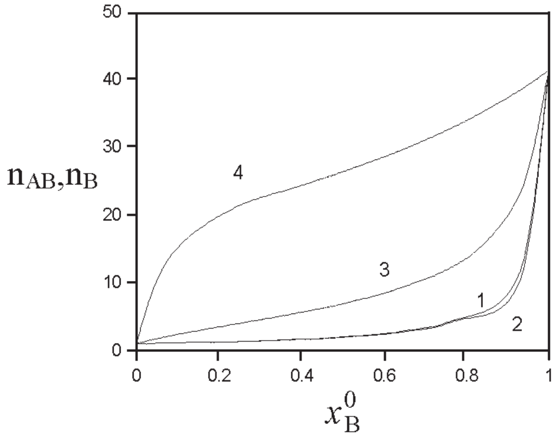


Fig. 2 Average number of association of mixture n_{AB} (lines 1, 2) and number of association of alcohol n_B (lines 3, 4) in tetrachloromethane-methanol mixture at T=293 K, x_B^0 is the mole fraction of methanol. Lines 2, 4 are calculated without allowance for solvation

tion. The solvation slightly increases the number of association n_{AB}, but decreases considerably the values n_B.

In the cyclohexanone–cyclohexanol and cyclohexanone–4-methylcyclohexanol mixtures with the same stoichiometry of aggregation due to the polarity of the solvating molecules of ketone a detailed description of the structure of the complexes of ketone with molecules and associates of alcohol was necessary [23, 24]. The permittivity of the cyclohexanone–cyclohexanol mixture was considered at ΔT=298–423 K and model gives a good reproduction of the experimental data. Complex formation and polarity of the ketone lead to a faster decrease of dipole factor on dilution of the alcohol compared with the above-considered mixtures of alcohol with non-polar solvent. The enthalpy of complex formation alcohol and ketone was found, ΔH_s= –23±8 kJ mol^{-1}, to coincide with the enthalpy of H-bonding in alcohol; the entropy of solvation is ΔS_s= –46±10 J mol^{-1} K^{-1}. Competition between processes of association and solvation yields a weak positive deviation from ideality. Solvation increases the number of association n_{AB} due to the fact that the enthalpy of complexation alcohol and ketone are very close, but greatly decrease the number of association of alcohol n_B in comparison with the cyclohexane–cyclohexanol mixture.

In general for all three types of alcohol solutions with positive deviation from ideality the quasichemical approach gives quite a good description of thermodynamic functions, permittivity, and coefficients of light scattering. In alcohol mixtures firstly the contribution of H-bonds to thermodynamic functions is comparable with those from the dipole and dispersion forces, and secondly, the number of association dramatically decreases on dilution, which generally results in a positive deviation from ideality.

The analysis of a set of physicochemical properties confirmed the ideas about the long-range molecular correlations in liquid self-organised by H-bonding [3, 4, 27]. In molecular liquids the supramolecular species are realised with the number of particles nearly ten and larger for quite normal parameters of liquid state. This result appears important for a new understanding of both the structure and properties of liquids.

Conclusions

The background of the unified quasichemical approach to thermodynamic, dielectric, and optical properties of molecular mixtures has been elaborated in general. The results presented demonstrate a way in which in a unified description a set of the physicochemical properties of mixtures can reflect the different molecular parameters, as well as quantitative analysis of the supramolecular ordering. Moreover a part of the results was obtained *a priori* creating a new possibility for predicting properties and design of liquid materials at the molecular-structural level. The methods developed can be employed to study supramolecular structure in many similar molecular systems. The importance of the quasichemical approach for investigating dynamic processes in molecular liquids may be mentioned. Firstly there is the theory of kinetic coefficients of non-equilibrium thermodynamics. Secondly there is the theory of relaxation acoustic, dielectric, spectra. Thirdly there is the application to kinetic processes occurring in liquids, e.g. to dynamics of the supramolecular reorganisation, an energy transfer, and intramolecular transitions.

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