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Anisotropic Inertial Term of the Solvation Energy in Binary Solutions

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Abstract—An expression based on the Fröhlich theorem is given for the anisotropic inertial solvation potential of solutions. The principle of the additivity of the anisotropic inertial solvation potentials of solution components is put forward and substantiated. A model thermodynamic function of the anisotropic inertial solvation potential of a binary solution is suggested. The effect of formation of 1 : 1 complexes and bimolecular associates on the anisotropic inertial solvation potential of a binary solution is analyzed. The composition dependences of the anisotropic inertial solvation potentials of binary solutions of nitrobenzene, acetonitrile, nitromethane, and tetrachloromethane in associated and nonassociated polar and nonpolar solvents and in water are determined. The dependences obtained are compared to the corresponding model functions. Changes in the contribution of specific intermolecular interactions to the anisotropic inertial term of the Helmholtz energy of solvation of binary solutions are revealed by this method. Previously unknown anisotropic inertial solvation potentials are obtained for associated and polar nonassociated liquids in relation to their content in hexane. Conclusions on the magnitude and character of changes in the microstructure of solutions are made. The transformation of the anisotropic inertial to isotropic noninertial term of the Helmholtz energy of solvation is noted by the example of a solution with the ethanol volume fraction in hexane of 0.13.

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The development of methods for studying the structure and properties of liquid solutions is one of basic problems of physical chemistry. This problem is extremely sophisticated, because the properties of solutions can differ essentially from those of their components owing to the occurrence of both universal and specific intermolecular interactions. All the known procedures for describing and calculating solution properties are based on certain models. Two different approaches, discrete and continual, can be distinguished in construction of these models.

The discrete approach usually implies setting the potentials of pair intermolecular interactions, written in the form of attraction and repulsion forces as functions of coordinates. It should be noted that all the numerous equations of interaction forces between pairs of molecules of the Lennard–Jones, Stockmeyer, Buckingham, Kihara, Kitaigorodskii, and other types are empirical, with no physical substantiation. Indeed, the potentials of intermolecular interactions are determined exclusively by Coulomb forces, but it is well known that in this case the dependences of both the attraction and repulsion forces on the distance should have the same dimension. Different character of these dependences is caused by replacement of actual distribution functions of the electron and nuclear density in a condensed medium by their rough approximation involving the use of one or two effective radii. The continual approach based on Onsager's model [1] does not use empirical pair potentials and eliminates the need for solving complex problems associated with their further summation. Even in the initial step of its application [2] it reduces to a minimum the number of empirical microparameters. In the next step [3–8], when it is based not on Onsager's model but on the electrostatic Fröhlich theorem [9], it does not involve empirical microparameters in calculation of the inertial anisotropic (dipole–dipole) term of the Helmholtz energy of solvation of molecules, associates, and complexes in solution. This version of the continual approach offers fundamentally new possibilities for optimizing physicochemical heterolytic reactions and revealing the mechanism of homeostasis and self-regulation of biological processes [10–13]. The possibility of operational separation of the solvation energy in liquids and solutions into the anisotropic and isotropic terms was substantiated in [3, 5, 7]. The possibility of rigorous calculation of the anisotropic inertial term of the solvation energy in solutions allows this term to be singled out and compared to model thermodynamic functions.

In [7] I presented an expression for the anisotropic inertial solvation potential of a liquid isotropic dielectric (I_{an}). In what follows, as in [7], it is often termed simply the anisotropic solvation potential

$$I_{\mathrm{an}} \equiv (\varepsilon_{\mathrm{s}} - n^2)(2\varepsilon_{\mathrm{s}} + n^2)3RT/\varepsilon_{\mathrm{s}}(n^2 + 2)^2. \tag{1}$$

Here ε_{s} and n are, respectively, the static dielectric constant and refractive index ($n \approx n_{\mathrm{D}} \approx \approx n_{\mathrm{f}}$) of the liquid.

It should be particularly emphasized that, according to the Fröhlich theorem [9], the expression obtained is universal and can be applied to both nonassociated and associated liquids (mixtures of monomers and associates), and also to solutions.

According to the approach being developed [3–8], a sphere containing in aggregate $\mathrm{N_A}$ molecules of components is mentally cut out from a solution that is a liquid homogeneous dielectric. In formation of a solution owing to intermolecular interactions of various kinds, the number of components in the sphere can change. The anisotropic inertial potential of a solution of the initial jth composition [$I_{\mathrm{an}(j)}$] always actually corresponds to the new composition and new structure of particles in the sphere cut out. It should be noted that the anisotropic inertial solvation potential of the sphere cut out is independent of the number of component particles in it. To simplify calculations, it is assumed that, in formation of a solution, the volume of the sphere incorporating $\mathrm{N_A}$ initial molecules remains constant, despite changes in the number and structure of the incorporated particles. Variation of $I_{\mathrm{an}(j)}$ of the sphere for different solution compositions is fully determined only by the new values of the dipole moments of all the particles incorporated in the sphere. The error arising from this assumption is insignificant.

As shown previously in [3], the electrooptical functions of solutions and components are interrelated by Eq. (2):

$$\Sigma\varphi_i(\varepsilon_{\mathrm{s}(j)} - n_{i(j)}{}^2)(2\varepsilon_{\mathrm{s}(j)} + n_{i(j)}{}^2)/\varepsilon_{s(j)}$$
$$= \Sigma\varphi_{i(j)}(\varepsilon_{i(j)} - n_{i(j)}{}^2)(2\varepsilon_{(j)i} + n_{i(\mathrm{j})}{}^2)/\varepsilon_{i(j)}\,, \tag{2}$$

where $\varphi_{i(j)}$ is the volume fraction of ith component in solution of jth composition; $\varepsilon_{\mathrm{s}(j)}$, $\varepsilon_{i(j)}$, and $n_{i(j)}$ are the static dielectric constants of solution of jth composition and of its components and the refractive indices of the components in the states corresponding to a given composition. If $\varepsilon_{\mathrm{s}(j)}$ noticeably exceeds $n_{i(j)}{}^2$ for any solution composition and the quantities n_i are close to each other, so that $n_{i(j)} \sim n_{(j)}$, expression (2) can be transformed into a simpler form:

$$(\varepsilon_{\mathrm{s}(j)} - n_{(j)}{}^2)(2\varepsilon_{\mathrm{s}(j)} + n_{(j)}{}^2)/\varepsilon_{\mathrm{s}(j)}$$
$$= \Sigma\varphi_{i(j)}(\varepsilon_{i(j)} - n_{i(j)}{}^2)(2\varepsilon_{i(j)} + n_{i(j)}{}^2)/\varepsilon_{i(j)}, \tag{3}$$

where $n_{(j)}$ is the refractive index of jth solution.

According to [3], relationship (3) can be represented as the sum of anisotropic potentials.

$$I_{\mathrm{an}(j)} = \Sigma\varphi_i I_{\mathrm{an},i(j)}\,. \tag{4}$$

Here

$$I_{\mathrm{an},i(j)} \equiv (\varepsilon_{i(j)} - n_{i(j)}{}^2)(2\varepsilon_{i(j)} + n_{i(j)}{}^2)3RT/\varepsilon_{i(j)}(n_{i(j)}{}^2 + 2)^2. \tag{5}$$

$I_{\mathrm{an}(j)}$ is the aggregate anisotropic solvation potential of N_{A} initial component molecules (taking into account all the forms of their coexistence) occurring in the mentally cut out spherical volume; $I_{\mathrm{an},i(j)}$ is the anisotropic solvation potential of $\mathrm{N_A}$ particles of ith component: in the form of molecules, associates, or complexes in the state exactly corresponding to their state in the jth solution composition. Expressions (2)–(4) physically substantiate the suggested principle of additivity of the anisotropic solvation potentials of the components in solution.

Consider the case of binary solutions consisting of components a and b, in which index $i \equiv$ a or b. Practically the composition dependence of the anisotropic solvation potential of a binary solution [expression (4)] is given by empirical relationship (6):

$$I_{\mathrm{an}(j)} = \Sigma\varphi_{i0(j)}\, I_{\mathrm{an},i(j)}, \tag{6}$$

where $I_{\mathrm{an}(j)}$ is the aggregate anisotropic solvation potential of a binary solution of jth composition; $\varphi_{i0(j)}$ is the initial volume fraction of ith component in solution of jth composition.

The model thermodynamic function of the anisotropic solvation potential of a binary solution ($I_{\mathrm{an}(\varphi)}$) has form (7):

$$I_{\mathrm{an}(j)} \equiv \Sigma\varphi_{i0(j)}I_{\mathrm{an},i} \tag{7}$$

where $\varphi_{i0(j)}$ are the initial volume fractions of ith component in solution of jth composition; $I_{\mathrm{an},i}$ are the anisotropic solvation potentials of N_A molecules of components a and b in the state of pure liquids:

$$I_{\mathrm{an,a}} \equiv (\varepsilon_{\mathrm{s,a}} - n_\mathrm{a}^2)(2\varepsilon_{\mathrm{s,a}} + n_\mathrm{a}^2)3RT/\varepsilon_{\mathrm{s,a}}(n_\mathrm{a}^2 + 2)^2,$$
$$I_{\mathrm{an,b}} \equiv (\varepsilon_{\mathrm{s,b}} - n_\mathrm{b}^2)(2\varepsilon_{\mathrm{s,b}} + n_\mathrm{b}^2)3RT/\varepsilon_{\mathrm{s,b}}(n_\mathrm{b}^2 + 2)^2.$$

Here $\varepsilon_{\mathrm{s,a}}$, n_a and $\varepsilon_{\mathrm{s,b}}$, n_b are the static dielectric constants and refractive indices of components a and b. Here and hereinafter, the anisotropic solvation potential of N_A molecules of a model thermodynamic function of the solution is printed bold. Equation (7), in contrast to (6), is strictly linear. Nonlinearity of experimental dependence (6) on the solution composition is indicative of changes in the contributions of various kinds of specific intermolecular interactions to the composition and energy of the solution formed. The value by which $I_{\mathrm{an}(j)}$ differs from $I_{\mathrm{an}(j)}$ allows calculation of changes in the contribution of specific intermolecular interactions to the energy of anisotropic solvation.

As an example of this approach, for solutions in which 1 : 1 complexes ab and associates b_2 are formed, let us compare the $I_{\mathrm{an}(\varphi)}$ values with the model function $I_{\mathrm{an}(j)}$. Consider the effect of formation of the complex ab in solution (by the scheme $\mathrm{a} + \mathrm{b} \rightleftarrows \mathrm{c}$) on the shape of the dependence of its potential $I_{\mathrm{an}(j)}$ on the composition. According to (4), we have

$$I_{\mathrm{an}(j)} = \varphi_{\mathrm{a}(j)}I_{\mathrm{an,a}} + \varphi_{\mathrm{b}(j)}I_{\mathrm{an,b}} + \varphi_{\mathrm{c}(j)}I_{\mathrm{an,c}}, \tag{8}$$

where $\varphi_{\mathrm{a}(\varphi)}$, $\varphi_{\mathrm{b}(\varphi)}$, and $\varphi_{\mathrm{c}(\varphi)}$ are the volume fractions of the components and complex in the solution; $I_{\mathrm{an,c}}$ is the anisotropic solvation potential of the complex. The volume fractions of molecules of components a and b in the solution can be given by expressions (9):

$$\varphi_{\mathrm{b}(j)} = \varphi_{\mathrm{b0}(j)} - \varphi_{\mathrm{bc}(j)} \text{ and } \varphi_{\mathrm{a}(j)} = \varphi_{\mathrm{a0}(j)} - \varphi_{\mathrm{ac}(j)}, \tag{9}$$

where φ_ac and φ_bc are the volume fractions corresponding to the components in the complexes. Substituting (9) in (8), we obtain Eq. (10):

$$I_{\mathrm{an}(j)} = \varphi_{\mathrm{a0}(j)}I_{\mathrm{an,a}} + \varphi_{\mathrm{b0}(j)}I_{an,\mathrm{b}} + \varphi_{\mathrm{c}(j)}[I_{\mathrm{an,c}} - (\varphi_{\mathrm{ac}(j)}/\varphi_{\mathrm{c}(j)})I_{\mathrm{an,a}} - (\varphi_{\mathrm{bc}(j)}/\varphi_{\mathrm{c}(j)})I_{\mathrm{an,b}}]. \tag{10}$$

Correspondingly, the volume fractions of the components and complex can be presented in the form of expressions (11) and (12):

$$\varphi_{\mathrm{a0}(j)} = \mathrm{N}_{\mathrm{a0}(j)}\mathrm{M}_\mathrm{a}/\rho_\mathrm{a}\mathrm{V}_{\Sigma(j)}, \tag{11}$$
$$\varphi_{\mathrm{b0}(j)} = \mathrm{N}_{\mathrm{b0}(j)}\mathrm{M}_\mathrm{b}/\rho_\mathrm{b}\mathrm{V}_{\Sigma(j)}, \tag{12}$$

where $N_{\mathrm{a0}(j)}$ and $N_{\mathrm{b0}(j)}$ are the initial mole fractions of the component molecules in the cut-out volume $\mathrm{V}_{\Sigma(j)}$ of jth solution.

$$\mathrm{V}_{\Sigma(j)} = [\mathrm{N}_{\mathrm{a}(j)}\mathrm{M}_\mathrm{a}/\rho_\mathrm{a} + \mathrm{N}_{\mathrm{b}(j)}\mathrm{M}_\mathrm{b}/\rho_\mathrm{b} + \mathrm{N}_{\mathrm{c}(j)}(\mathrm{M}_\mathrm{a} + \mathrm{M}_\mathrm{b})/\rho_\mathrm{c}]$$
$$\mathrm{N}_{\mathrm{a}(j)} + \mathrm{N}_{\mathrm{b}(j)} + \mathrm{N}_{\mathrm{c}(j)} = 1. \tag{13}$$

Here $\mathrm{V}_{\Sigma(j)}$ is equal to the volume of sphere in solution of jth composition, incorporating 1 mol of particles of the initial components $\mathrm{a}_{0(j)}$ and $\mathrm{b}_{0(j)}$ (the sphere volume depends on the solution composition); ρ_a, ρ_b, and ρ_c are the densities of the components and complex; M_a and M_b are the molecular weights of the components.

$$\rho_\mathrm{c} = (\mathrm{M}_\mathrm{a} + \mathrm{M}_\mathrm{b})/(\mathrm{M}_\mathrm{a}/\rho_\mathrm{a} + \mathrm{M}_\mathrm{b}/\rho_\mathrm{b}), \tag{14}$$

$$\varphi_{\mathrm{c}(j)} = \mathrm{N}_{\mathrm{c}(j)}(\mathrm{M}_\mathrm{a} + \mathrm{M}_\mathrm{b})/\rho_\mathrm{c}\mathrm{V}_{\Sigma(j)}, \tag{15}$$

$$\varphi_{\mathrm{ac}(j)} = \mathrm{N}_{\mathrm{c}(j)}\mathrm{M}_\mathrm{a}/\rho_\mathrm{a}\mathrm{V}_{\Sigma(j)}, \tag{16}$$
$$\varphi_{\mathrm{bc}(j)} = \mathrm{N}_{\mathrm{c}(j)}\mathrm{M}_\mathrm{b}/\rho_\mathrm{b}\mathrm{V}_{\Sigma(j)}. \tag{17}$$

Here $\mathrm{N}_{\mathrm{c}(j)}$ is the mole fraction of the complex.

It should be noted that the ratios ($\varphi_{\mathrm{ac}(j)}/\varphi_{\mathrm{c}(j)}$) and ($\varphi_{\mathrm{bc}(j)}/\varphi_{\mathrm{c}(j)}$) are composition-independent. Using relationships (8)–(17), we obtain

$$I_{\mathrm{an}(j)} = \varphi_{\mathrm{a0}(j)}I_{\mathrm{an,a}} + \varphi_{\mathrm{b0}(j)}I_{\mathrm{an,b}} + \varphi_{\mathrm{c}(j)}\{I_{\mathrm{an,c}} - [\rho_\mathrm{c}M_\mathrm{a}/(\mathrm{M}_\mathrm{a} + \mathrm{M}_\mathrm{b})\rho_\mathrm{a})I_{\mathrm{an,a}} - (\rho_\mathrm{c}M_\mathrm{b}/(\mathrm{M}_\mathrm{a} + \mathrm{M}_\mathrm{b})\rho_\mathrm{b}]I_{\mathrm{an,b}}\}. \tag{18}$$

The complexation constant is given in the form

$$K_\mathrm{c} = [\mathrm{c_c}]_{(j)}/([\mathrm{c_{a,0}}]_{(j)} - [\mathrm{c_c}]_{(j)})([\mathrm{c_{b,0}}]_{(j)} - [\mathrm{c_c}]_{(j)}), \tag{19}$$

where $[\mathrm{c_c}]_{(j)}$, $[\mathrm{c_{a0}}]_{(j)}$, and $[\mathrm{c_{b0}}]_{(j)}$ are the molar concentrations of the complex and components in jth solution, equal to: $[\mathrm{c_c}]_{(j)} = \mathrm{N}_{\mathrm{c}(j)}/\mathrm{V}_{\Sigma(j)}[\mathrm{c_{a0}}]_{(j)} = \mathrm{N}_{\mathrm{a0}(j)}/\mathrm{V}_{\Sigma(j)}$, $[\mathrm{c_{b0}}]_{(j)} = \mathrm{N}_{\mathrm{b0}(j)}/\mathrm{V}_{\Sigma(j)}$.

Transforming expression (19) taking into account (11)–(13) and (15), we obtain

$$K_\mathrm{c}(\mathrm{M}_\mathrm{a} + \mathrm{M}_\mathrm{b})\rho_\mathrm{a}\rho_\mathrm{b}/\mathrm{M}_\mathrm{a}\mathrm{M}_\mathrm{b}\rho_\mathrm{c} = \varphi_{\mathrm{c}(j)}/(\varphi_{\mathrm{a0}(j)} - \varphi_{\mathrm{c}(j)})(\varphi_{\mathrm{b0}(j)} - \varphi_{\mathrm{c}(j)}). \tag{20}$$

Introducing a new designation

$$K_\varphi \equiv \varphi_{\mathrm{c}(j)}/(\varphi_{\mathrm{a0}(j)} - \varphi_{\mathrm{c}(j)})(\varphi_{\mathrm{b0}(j)} - \varphi_{\mathrm{c}(j)}). \tag{21}$$

and combining (20) and (21), we obtain

$$K_\varphi = K_\mathrm{c}(\mathrm{M}_\mathrm{a} + \mathrm{M}_\mathrm{b})\rho_\mathrm{a}\rho_\mathrm{b}/(\mathrm{M}_\mathrm{a}\mathrm{M}_\mathrm{b})\rho_\mathrm{c}. \tag{22}$$

Note that K_φ and K_c have similar properties, i.e., are concentration-independent. By solving Eq. (21) for φ_c, we obtain

$$\varphi_{\mathrm{c}(j)} = [(1 + K_\varphi)/(2K_\varphi)] - \{[(1 + K_\varphi)/(2K_\varphi)]^2 - \varphi_{\mathrm{a0}(j)}{*}\varphi_{\mathrm{b0}(j)}\}^{0.5}. \tag{23}$$

Finally, we obtain

$$\begin{aligned} I_{\mathrm{an(j)}} &= \varphi_{\mathrm{a0(j)}} I_{\mathrm{an,\,a}} + \varphi_{\mathrm{b0(j)}} I_{\mathrm{an,\,b}} \\ &+ ([(1 + K_\varphi)/(2K_\varphi)] - \{[(1 + K_\varphi)/(2K_\varphi)]^2 - \varphi_{\mathrm{a0(j)}} {*} \varphi_{\mathrm{b0(j)}}\}^{0.5})\cdot \\ &\{I_{\mathrm{an,\,c}} - [\rho_{\mathrm{c}} M_{\mathrm{a}}/(\mathrm{M_a} + \mathrm{M_b})\rho_{\mathrm{a}}] I_{\mathrm{an,\,a}} \\ &- [\rho_{\mathrm{c}} M_{\mathrm{b}}/(\mathrm{M_a} + \mathrm{M_b})\rho_{\mathrm{b}}] I_{\mathrm{an,\,b}}\}. \end{aligned} \tag{24}$$

The sought-for expression determining the difference of the potentials of solutions in which complexes are formed from the model functions is as follows:

$$\Delta I_{\mathrm{an(j)}} = I_{\mathrm{an(j)}} - \mathbf{I}_{\mathrm{an(j)}}. \tag{25}$$

Using (7) and (18), we obtain for the case of formation of complex ab (assuming that the free component molecules in solutions of different compositions do not change their anisotropic potentials)

$$\begin{aligned} &\Delta I_{\mathrm{an(j)}}/\{I_{\mathrm{an,\,c}} - [\rho_{\mathrm{c}} M_{\mathrm{a}}/(\mathrm{M_a} + \mathrm{M_b})\rho_{\mathrm{a}}] I_{\mathrm{an,\,a}} \\ &- [\rho_{\mathrm{c}} M_{\mathrm{b}}/(\mathrm{M_a} + \mathrm{M_b})\rho_{\mathrm{b}}] I_{\mathrm{an,\,b}}\} = \varphi_{\mathrm{c(j)}}. \end{aligned} \tag{26}$$

As seen from relationships (26), the shape of the dependence of $\Delta I_{\mathrm{an(j)}}$ on the solution composition is described by function $\varphi_{\mathrm{c(j)}}$. In the form normalized with respect to maximum, relationship (26) takes the form

$$\begin{aligned} \Delta I_{an\mathrm{(j)}}/\Delta I_{an,\,\mathrm{max}} &= ([(1 + K_\varphi)/(2K_\varphi)] - \{[(1 + K_\varphi)/(2K_\varphi)]^2 \\ &- \varphi_{\mathrm{a0(j)}}\varphi_{\mathrm{b0(j)}}\}^{0.5})/([(1 + K_\varphi)/(2K_\varphi)] \\ &- \{[(1 + K_\varphi)/(2K_\varphi)]^2 - 0.25\}^{0.5}). \end{aligned} \tag{27}$$

Here

$$\begin{aligned} \Delta I_{\mathrm{an,\,max}} &= ([(1 + K_\varphi)/(2K_\varphi)] - \{[(1 + K_\varphi)/(2K_\varphi)]^2 - 0.25\}^{0.5})\cdot \\ &\{I_{\mathrm{an,\,c}} - [\rho_{\mathrm{c}} M_{\mathrm{a}}/(\mathrm{M_a} + \mathrm{M_b})\rho_{\mathrm{a}}] I_{\mathrm{an,\,a}} \\ &- [\rho_{\mathrm{c}} M_{\mathrm{b}}/(\mathrm{M_a} + \mathrm{M_b})\rho_{\mathrm{b}}] I_{\mathrm{an,\,b}}\}. \end{aligned} \tag{28}$$

The quantities K_φ and $I_{\mathrm{an,\,c}}$ in the case of formation of complex ab can be estimated by least-squares fitting of the experimental and theoretical composition dependences [relationships (26) and (27)] .

The dependences of $\Delta I_{\mathrm{an(j)}}$ on the solution composition at various K_φ [calculated from Eqs. (23) and (26)] are plotted in Fig. 1. It can be seen that an increase in K_φ leads to a change from the bell-shaped to pyramidal dependence. The coordinate of the maximum remains constant and equal to 0.5. When only 2:1 or only 1:2 complexes are formed in solution, the position of the maximum shifts toward φ_{b0} 0.25 or 0.75.

Consider an example when one of the components can form associates by the scheme b + b ⇄ b2. Let us note an important feature of associated liquids: the capability to change the ratio of monomers and associates and hence the anisotropic solvation potential in solutions of various compositions. The composition dependence of $I_{\mathrm{an(j)}}$ of solution in this example is described by Eq. (29) based on the principle of additivity of the anisotropic solvation potentials of all the components:

$$I_{an\mathrm{(j)}} = \varphi_{\mathrm{a0(j)}} I_{\mathrm{an,\,a}} + \varphi_{\mathrm{b1(j)}} I_{\mathrm{an,\,b1}} + \varphi_{\mathrm{b2(j)}} I_{\mathrm{an,\,b2}}, \tag{29}$$

where $\varphi_{\mathrm{b1(j)}}$ and $I_{\mathrm{an,\,b1}}$ are the volume fraction and anisotropic solvation potential of the monomer, and $\varphi_{\mathrm{b2(j)}}$ and $I_{\mathrm{an,\,b2}}$ are those of the dimer.

Taking into account that $\varphi_{\mathrm{b0(j)}} = \varphi_{\mathrm{b2(j)}} + \varphi_{\mathrm{b1(j)}}$, we obtain

$$I_{an\mathrm{(j)}} = \varphi_{\mathrm{a0(j)}} I_{\mathrm{an,\,a}} + \varphi_{\mathrm{b0(j)}} I_{\mathrm{an,\,b1}} + \varphi_{\mathrm{b2(j)}}(I_{\mathrm{an,\,b2}} - I_{\mathrm{an,\,b1}}). \tag{30}$$

The quantity $\Delta I_{an\mathrm{(j)}}$ in the above example is given by

$$\begin{aligned} \Delta I_{\mathrm{an(j)}} &= \varphi_{\mathrm{a0(j)}} I_{\mathrm{an,\,a}} + \varphi_{\mathrm{b0(j)}} I_{\mathrm{an,\,b1}} \\ &+ \varphi_{\mathrm{b2(j)}}(I_{\mathrm{an,\,b2}} - I_{\mathrm{an,\,b1}}) - \mathbf{I}_{\mathrm{an(j)}}, \\ \mathbf{I}_{\mathrm{an(j)}} &= \varphi_{\mathrm{a0(j)}} I_{\mathrm{an,\,a}} + \varphi_{\mathrm{b0(j)}} I_{\mathrm{an,\,b(j)}}. \end{aligned} \tag{31}$$

In this relationship, the variable $I_{\mathrm{an,b(j)}}$ is given by Eq. (32) based on the additivity principle:

$$\mathbf{I}_{\mathrm{an,\,b(j)}} = \varphi_{\mathrm{b1(j=1)}} I_{\mathrm{an,\,b1}} + \varphi_{\mathrm{b2(j=1)}} I_{\mathrm{an,\,b2}}, \tag{32}$$

where $\varphi_{\mathrm{b1(j=1)}}$ and $\varphi_{\mathrm{b2(j=1)}}$ are the volume fractions of the monomer and dimer in component b as a pure liquid. By combining (31) and (32), we obtain the sought-for relationship for the jth solution composition in the case when component b forms dimers:

$$\Delta I_{\mathrm{an(j)}} = (I_{\mathrm{an,\,b2}} - I_{\mathrm{an,\,b1}})(\varphi_{\mathrm{b2(j)}} - \varphi_{\mathrm{b0(\varphi)}}\varphi_{\mathrm{b2(\varphi=1)}}). \tag{33}$$

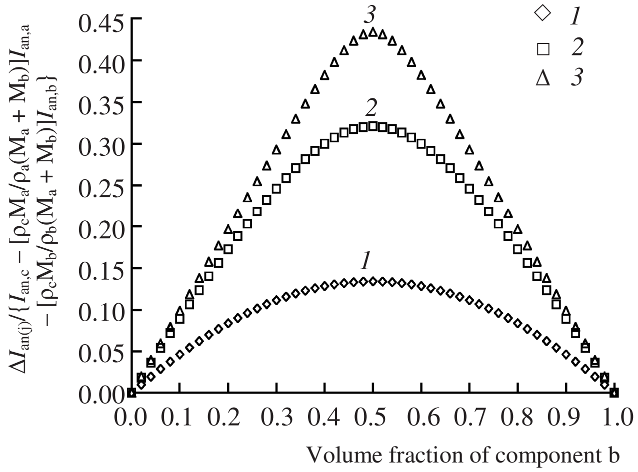

Fig. 1. Dependences of the difference between the functions of the anisotropic solvation potentials of binary systems in the case of formation of 1:1 complexes and those of their model potentials on the solution composition and complexation constant K_φ. K_φ: (*1*) 1, (*2*) 10, and (*3*) 100.

Let us transform Eq. (33) to the form

$$\Delta I_{an(\varphi)}/(I_{\mathrm{an,\,b2}} - I_{\mathrm{an,\,b1}}) = (\varphi_{\mathrm{b2}(\varphi)} - \varphi_{\mathrm{b0}(\varphi)}\cdot\varphi_{\mathrm{b2}(\varphi=1)}). \qquad (34)$$

The quantity φ_{b2} in expression (34) is given by

$$\varphi_{\mathrm{b2(j)}} = \mathrm{N_{c(j)}2M_b/\rho_b V_{\Sigma(j)}}. \qquad (35)$$

The association constant in this case is defined as

$$K_{\mathrm{c}} = [\mathrm{c_{b2}}]_{\mathrm{(j)}}/([\mathrm{c_{b0}}]_{\mathrm{(j)}} - 2[\mathrm{c_{b2}}]_{\mathrm{(j)}})^2. \qquad (36)$$

The factor 2 in Eqs. (35) and (36) takes into account the fact that one associate particle is formed from two molecules of component b.

By transformations similar to (19)–(22), we obtain Eq. (37):

$$K_\varphi = \varphi_{\mathrm{b2(j)}}/(\varphi_{\mathrm{b0(j)}} - \varphi_{\mathrm{b2(j)}})^2 = K_{\mathrm{c}}2\rho_{\mathrm{b}}/\mathrm{M_b}, \qquad (37)$$

whence follows

$$\varphi_{\mathrm{b2(j)}} = (\varphi_{\mathrm{b0(j)}} + 1/2\ K_\varphi) - [(\varphi_{\mathrm{b0(j)}} + 1/2\ K_\varphi)^2 - \varphi_{\mathrm{b0(j)}}{}^2]^{0.5}. \qquad (38)$$

The quantity K_φ can be calculated by least-squares fitting of the experimental and theoretical dependences of $\Delta I_{\mathrm{an}(\varphi)}$ on the composition in the case of association.

The model dependences under consideration are shown in Fig. 2. According to (34) and (38), these functions are unsymmetrical, and the position of the maximum is shifted with increasing K_φ. For example, at K_φ 1 the maximum is observed at φ_{b0} 0.40, and at K_φ 10 and 100, at φ_{b0} 0.48 and 0.50, respectively. In contrast to the dependences observed in the case of formation of a complex (Fig. 1), the ordinate of the maximum of the functions under consideration [Eq. (34)] decreases with increasing K_φ, tending to zero.

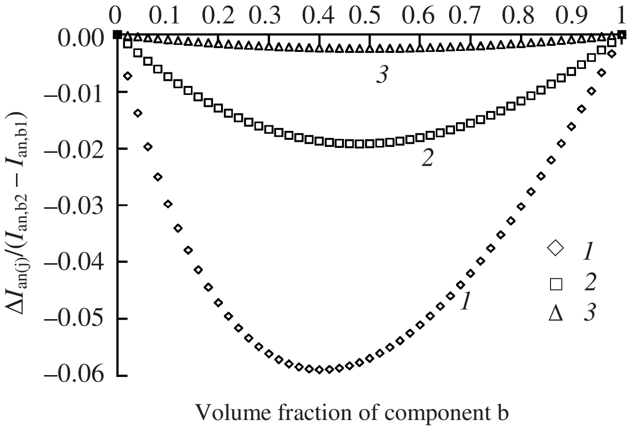

Fig. 2. Dependences of the difference between the functions of the anisotropic solvation potentials of the binary systems in the case of dimer formation and those of their model potentials on the solution composition and association constant. K_φ: (*1*) 1, (*2*) 10, and (*3*) 100.

For the passive component a, the anisotropic solvation potential $I_{\mathrm{an,a}}$ remains constant at all the compositions, and $I_{\mathrm{an,b(j)}}$ can be determined by Eq. (39).

$$I_{\mathrm{an,\,b(j)}} = [I_{\mathrm{an(j)}} - I_{\mathrm{an,\,a}}(1 - \varphi_{\mathrm{b0(j)}}]/\varphi_{\mathrm{b0(j)}}. \qquad (39)$$

Here the quantity $I_{\mathrm{an,\,b(j)}}$ is described by an expression similar to (4):

$$I_{\mathrm{an,\,b\,(j)}} = \Sigma\tilde{\omega}_{\mathrm{i\,b(j)}}I_{\mathrm{an,i(j)}}$$
$$\equiv N_A[\tilde{\omega}_{\mathrm{1b(j)}}(\mu^2/\mathrm{r_{str}}^3)_{\mathrm{1b}} + \ldots + \tilde{\omega}_{\mathrm{1n(j)}}(\mu^2/\mathrm{r_{str}}^3)_{\mathrm{nb}}],\ (\mathrm{i} = [1\ldots\mathrm{n}]),\ (40)$$

where $(\mu^2/\mathrm{r_{str}}^3)_{\mathrm{1b}}$ and $(\mu^2/\mathrm{r_{str}}^3)_{\mathrm{nb}}$ are the mean ratios of the squares of the dipole moments of the monomer and associates consisting of two to *n* molecules to the cubes of the corresponding structural radii (with averaging performed over all possible isomers); $\tilde{\omega}_{\mathrm{1b(j)}}$, $\ldots,\tilde{\omega}_{\mathrm{nb(j)}}$ are the probabilities of their occurrence in the *j*th solution.

Let us consider in more detail the physical sense of the parameter $I_{\mathrm{an,\,b(j)}}$. For this purpose, let us multiply and divide term by term the right side of Eq. (40) by the ratio $\mathrm{r_{str,1b}}^3/\mathrm{r_{str,1b}}^3$ and take the factor $1/\mathrm{r_{str,1b}}^3$ outside the common brackets. Then, taking into account that the ratio $\mathrm{r_{str,ib}}^3/\mathrm{r_{str,1b}}^3$ within the error limits is equal to the number of molecules in the associate, we obtain expression (41):

$$N_A^{-1}I_{\mathrm{an,\,b(j)}} = [\tilde{\omega}_{\mathrm{1b(j)}}\mu_{\mathrm{1b}}{}^2 + \tilde{\omega}_{\mathrm{2b(j)}}(\mu_{\mathrm{2b}}{}^2/2) + \ldots + \tilde{\omega}_{\mathrm{1n(j)}}(\mu_{\mathrm{n\,b}}{}^2/\mathrm{n})]/\mathrm{r_{str,1b}}^3$$
$$= <\mu_{\mathrm{1b}}{}^2>_{\mathrm{(j)}}/\mathrm{r_{str,1b}}^3 \equiv \mu_{\mathrm{1b}}{}^2/\alpha_{\mathrm{an1b(j)}}{}^3, \qquad (41)$$

where $<\mu_{\mathrm{1b}}{}^2>_{\mathrm{(j)}}$ is the mean dipole moment squared (counting on vacuum) per molecule b in solution, taking into account all its possible species, μ_{1b} is the dipole moment of molecule b in a vacuum, and $\alpha_{\mathrm{an1b(j)}}$ is its effective radius of anisotropic intermolecular interactions in *j*th solution (Onsager radius).

To check the efficiency of this approach, let us compare (assuming the additivity of the anisotropic potentials of the solution components) the concentration dependences of the quantities $I_{\mathrm{an(j)}}$ found experimentally using Eq. (4) and of the quantities $\boldsymbol{I}_{\mathrm{an(j)}}$ (model) calculated by Eq. (7). Figures 3–6 show the experimental dependences of $I_{\mathrm{an(j)}}$ on the compositions of solutions of polar and nonpolar associated and nonassociated organic liquids and of water in nitrobenzene, acetonitrile, nitromethane, and tetrachloromethane at room temperatures, obtained on the basis of reference data [14, 15]. It should be reminded that the relative accuracy of determining I_{an}

in a liquid and $I_{\text{an,b(j)}}$ in a solution depends on the accuracy of determining ε_s and even for low-polarity substances usually does not exceed 2%, decreasing with an increase in the polarity.

For nitrobenzene solutions (Fig. 3), the concentration dependences of $I_{\text{an(j)}}$ are mostly linear, except the solutions in aniline and p-xylene. However, even for solutions of nitrobenzene in aniline, with quite opposite chemical properties of the components, the maximal value of $\Delta I_{\text{an(j)}}$ does not exceed kT. The shape of the composition dependence of ΔI_{an} for the solutions in aniline, with a maximum at approximately φ_{b0} ~0.5, suggests both the formation of weak complexes with the $I_{\text{an,ab}}$ value lower than in nitrobenzene and the decomposition of weak associates. Final conclusions cannot be made without more detailed concentration dependences. The results obtained show that α_{an}^3, the cube of the Onsager radius of nitrobenzene, remains approximately constant in the solutions under consideration. The changes do not exceed 10% even for solutions in aniline.

As seen from Fig. 4, the experimental dependences of $I_{\text{an(j)}}$ for solutions of acetonitrile in water and organic liquids are linear. However, small positive deviations (within kT) are observed with water at φ_{b0} ~0.2. Apparently, in these solutions the number of cyclic associates of water decreases. Comparison of the dependences for the solutions in acetonitrile and nitromethane, which are close in polarity (the anisotropic solvation potentials of these liquids are 36.8 and 35.9 kJ mol^{-1}, respectively), shows that they are essentially different (Fig. 5). For example, nitromethane owing to its acid properties forms weak 1:1 complexes with all the alcohols, with the strongest complexes formed with 1-propanol. The quantities $\Delta I_{\text{an (j)}}$ for the solutions under consideration are given in Table 1. However, it can be seen that the strongest changes in $I_{\text{an(j)}}$ are observed with benzene rather than with alcohols. The results obtained suggest formation of a charge-transfer complex of type II [16–18].

The concentration dependence of $I_{\text{an(j)}}$ for chloroform, tetranitromethane, and benzene in tetrachloromethane (Fig. 6) are linear. These facts confirm the applicability of the principle of additivity of anisotropic potentials to solutions formed by components of very low polarity such as, e.g., CCl_4, whose nonzero polarity is caused by the presence of molecules in an excited vibration state with the nonzero dipole moment. In solutions of

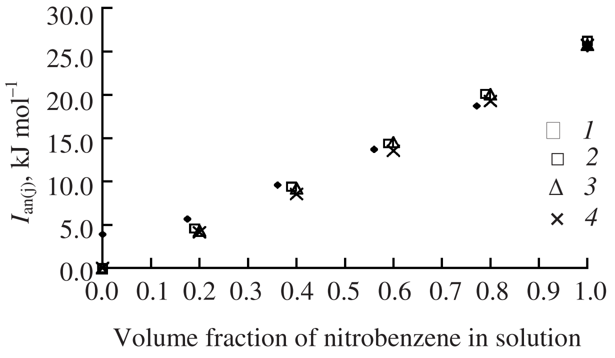

Fig. 3. Composition dependences of the anisotropic solvation potentials of solutions of nitrobenzene in organic liquids: (*1*) aniline, (*2*) hexane, (*3*) cyclohexane, and (*4*) *p*-xylene.

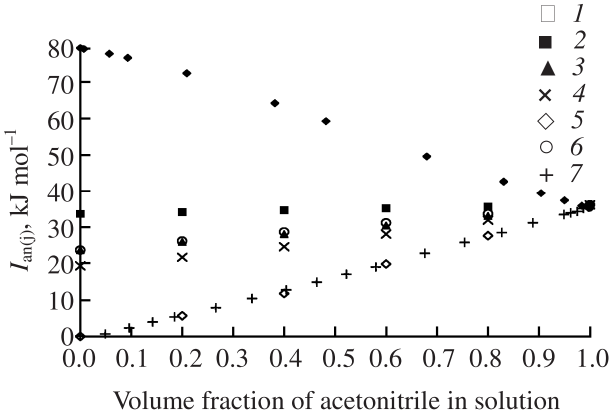

Fig. 4. Composition dependences of the anisotropic solvation potentials of solutions of acetonitrile in organic liquids: (*1*) water, (*2*) methanol, (*3*) ethanol, (*4*) 1-propanol, (*5*) benzene, (*6*) acetone, and (*7*) tetrachloromethane.

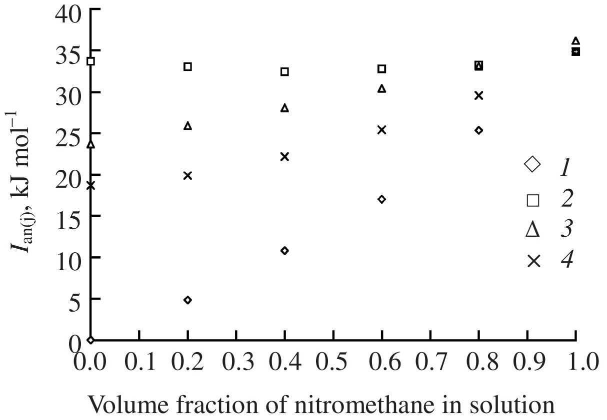

Fig. 5. Composition dependences of the anisotropic solvation potentials of solutions of nitromethane in organic liquids: (*1*) benzene, (*2*) methanol, (*3*) ethanol, and (*4*) 1-propanol.

Table 1. Difference between the experimental and calculated values of ΔI_{an} (kJ mol^{-1}) for solutions of nitromethane in organic solvents at 20°C

Volume fraction of nitromethane in solution	Benzene	Methanol	Ethanol	1-Propanol
0	0.00	0.00	0.00	0.00
0.2	–2.15	–0.90	–0.28	–2.02
0.4	–3.16	–1.74	–0.63	–2.95
0.6	–3.94	–1.63	–0.77	–2.96
0.8	–2.54	–1.40	–0.60	–2.06
1	–0.01	0.00	0.00	0.00

tetranitromethane in CCl_4, the concentration dependences also suggest the presence of polar species formed by partial dissociation of tetranitromethane even in the neat liquid [19].

Table 2. Dependence of the anisotropic solvation potentials $I_{an,b}$ (kJ mol^{-1}) of organic compounds (b) on the composition of solutions in hexane at 20 and 25°C

Volume fraction of b	Ethanol	1-Butanol	Acetone	Benzonitrile	Nitro-benzene
0.01	9.9				
0.03	5.8				
0.04		3.8			
0.05	5.9		25.6		
0.08					
0.09		3.7			
0.10	9.2				
0.11			25.3		
0.12		3.7			
0.13	0.9				
0.16		4.1			
0.17			24.1		
0.19					24.0
0.20		5.4		21.0	
0.24			23.3		
0.29		8.0			
0.3					
0.31			22.9		
0.36		10.8			
0.38			22.7		
0.39					24.1
0.40				20.8	
0.42	17.0				
0.45		12.3			
0.46			22.5		
0.55			22.2		
0.59					24.4
0.60				20.4	
0.65			19.9		
0.69	20.6				
0.76			21.2		
0.79					25.4
0.80				19.8	
0.85	21.7				
0.87			20.6		
0.88		14.8			
1.00	22.5	15.0	20.0	19.0	26.2

The quantities $I_{an,b(j)}$ for solutions of organic substances in hexane, calculated by Eq. (39), are given in Table 2. It can be seen that significant changes in the structure of component b are observed with alcohols. With an increase in the volume fraction of ethanol from 0 to 0.13, the ethanol molecules form cyclic associates of various structures with the dipole moment close to zero. The relative content of these species is noticeable at φ_{b0} ~0.045, and at φ_{b0} ~0.13 these species prevail. The formation of cyclic associates is also observed in solutions of 1-butanol in hexane, with the maximal content at φ_{b0} ~0.10. For acetone and benzonitrile, there is a weak but characteristic trend toward a decrease in $I_{an,b(j)}$ with increasing volume fraction of the polar component. In acetone, the magnitude of this effect is two times greater than in benzonitrile, probably because of the higher chemical activity of acetone. A decrease in $I_{an,b(j)}$ is due to the formation of weak sandwich-type dimers. Nitrobenzene behaves differently, also forming weak dimers but of the type of charge-transfer complexes.

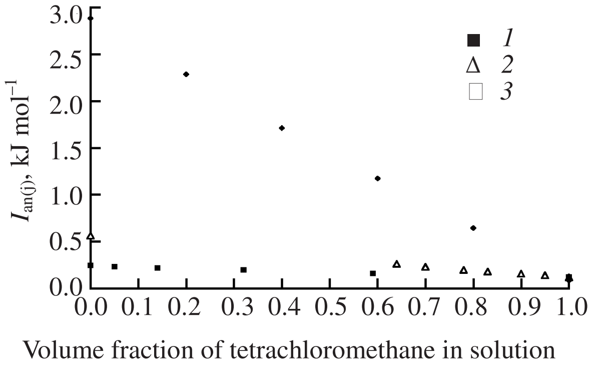

Fig. 6. Composition dependences of the anisotropic solvation potentials of solutions of tetrachloromethane in (*1*) benzene, (*2*) tetranitromethane, and (*3*) chloroform.

In Table 3, the composition dependences of $I_{an,b(j)}$ for solutions of ethanol in hexane are given at essentially different temperatures. It is interesting that, in the concentration range where the content of cyclic associates is maximal, variation of the temperature affects $I_{an,b(j)}$ very weakly, which suggests a particular, nonentropic character of changes in the solution structure. In the regions of existence of acyclic associates at both low and limiting concentrations of ethanol, the energy of anisotropic intermolecular interactions varies with temperature significantly. It was noted previously that hydrogen bonding makes a noticeable contribution to the energy of isotropic intermolecular interactions [7, 20]. The formation of cyclic associates is accompanied by an appreciable decrease in the anisotropic term of the Helmholtz energy of intermolecular interactions of ethanol molecules with the medium ($F_{\mathrm{an,b(j)}}$), from –9.5 kJ mol^{-1} for the model solution at φ_{b0} 0.13 (Λ_ε 422) to –0.2 kJ mol^{-1} for the real solution of the same composition (Λ_ε 0.215). In accordance with the law of energy conservation, taking into account a small change in the enthalpy of the solution of the composition φ_{b0} 0.13, it can be stated that the process is accompanied by an increase, equal in magnitude, in the isotropic term of the solvation energy in solution. The data obtained allow estimation of this value. High static dielectric constant of associated liquids is largely due to correlations in the collective processes of proton hopping along hydrogen bonds, but the relaxation time of the main polarization processes is determined by the slow motion of heavy nuclei of the molecules. Noticeable, and equal in magnitude, increase in the contribution of the high-frequency noninertial isotropic term to the intermolecular interaction energy is caused by an increase in the role of excited states of hydrogen bonds (at the moment of proton hopping) [21] in cyclic alcohol associates. The above-noted change in the solution structure at φ_{b0} 0.13 can be considered as a new phenomenon differing from phase transition of the second kind.

On the whole, the results obtained demonstrate new opportunities offered by the dielcometric method of solution analysis. Namely, it is possible to quantitatively single out and determine the magnitude of changes in the contribution to the energy of solvation, made by anisotropic specific intermolecular interactions, i.e., by intermolecular interactions caused by redistribution of the nuclear charge between the interacting molecules in the solution. This, in turn, furnishes information not only on the possibility of the occurrence of a heterolytic reaction in a solution, but also on the reaction mechanism [19].

Table 3. Temperature and composition dependences of the anisotropic solvation potential of ethanol $I_{\mathrm{an,b}}$ (kJ mol^{-1}) in hexane solutions

Volume fraction of ethanol	–80°C	20°C	50°C
0.007	20.5	9.9	9.4
0.027	8.5	5.8	6.1
0.045	8.1	5.9	5.9
0.105	15.9	9.2	7.8
0.133	**1.3**	**0.9**	**0.9**
0.420		17.0	13.8
0.685	39.4	20.6	17.0
0.848	41.2	21.7	18.0
1.000	42.6	22.5	18.9

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