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Structure and Properties of Acetone Solvates in Binary Mixtures with Some Nonpolar Solvents

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Abstract—Variations of short-range molecular interactions in acetone–nonpolar solvent systems have been evaluated, and the nature of these variations has been determined in terms of a new continual parameter-free approach to modeling the structure and properties of binary liquid nonelectrolyte mixtures. The results have been obtained by comparing the experimental heats of mixing of acetone with nonpolar solvents with the calculated changes in the energy of solvation in analogous model systems. The theoretical and experimental data suggest formation of azeotrope and demonstrate the effect role of short-range intra- and intermolecular interactions on the azeotrope parameters. No symmetry has been found in the differences between the compositions of solvation shells of acetone molecules and nonpolar counterparts as compared to the solvation shell compositions typical of mixtures formed by only polar or only nonpolar solvents.

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The present article reports on the applicability of a new version of the continual parameter-free approach [1–11] to the evaluation and determination of the nature of variation of short-range molecular interactions in acetone–nonpolar solvent systems. The data were obtained by comparing the heats of mixing of real liquids with the calculated changes of solvation energy in analogous model systems [10]. Unlike real mixtures, short-range molecular interactions in model systems are anchored to the initial components, and no other molecular interactions are possible. It should be noted that the *g*-factor value of acetone, which characterizes the contribution of short-range molecular interactions to polarization of a dielectric by electrostatic field [8], is equal to 1.41 at 20°C; it occupies an intermediate place between aprotic and protic liquids (1.06 for nitromethane, 0.74 for chlorobenzene, 3.03 for propan-2-ol, and 2.25 for phenol). This confirms the ability of acetone molecules to undergo enolization.

The physicochemical and thermodynamic parameters of the initial components (20°C) are given in Table 1. The thermodynamic solvation parameters [10] necessary for the calculations and plotting of diagrams are collected in Tables 2 and 3. Figures 1–5 show the thermodynamic solvation functions in model acetone–nonpolar solvent mixtures and the experimental heats of mixing for four systems [12]. In all figures, italicized numerals *1* and *2* denote the mole fractions of self-associates [$m_{(a)a}$, $m_{(b)b}$], *3* and *4* denote the mole fractions of mixed solvates [$m_{(a)b}$, $m_{(b)a}$]; *5* stands for the total variation of the internal energy of solvation in model system [$\Sigma\delta\Delta F(\varphi_b)/RT$], *6* denotes the experimental molar heats of mixing ($\Delta H_{exp}/RT$), and *7* corresponds to the calculated molar change of the contribution of short-range molecular interactions to the energy of intermolecular interactions upon mixing ($\Sigma\Delta H_{SRMI}/RT$). The energies are given in *RT* units.

In all the examined mixtures, predominant self-association of acetone and nonpolar component is clearly seen from the coordinates of the corresponding inverse solvation points ($\varphi_{bi} < 0.5$, $\varphi_{ai} >> 0.5$), where both acetone and nonpolar solvent occupy approximately equal volumes in their solvation shells. In an ideal solution, $\varphi_{ai} = \varphi_{bi} = 0.5$; for systems where mixed solvates are considerably more stable than self-associates, $\varphi_{ai} \rightarrow 0$, $\varphi_{bi} > 1$, and in the opposite case, $\varphi_{ai} > 1$, $\varphi_{bi} > 0$ [10].

In a series of mixtures with the same solute, the quantity φ_{bi} characterize the competitive ability of nonpolar molecule to replace acetone molecule from the solva-

Table 1. Some characteristics of the solvents used[a]

Solvent	M	n_D^{20}	ε_S	ρ, g/cm^3	Λ_n	Λ_ε	ΔH_v^0, kJ/mol	I_{an}, kJ/mol	I_{is}, kJ/mol	$r_{str}^3 \times 10^{24}$, cm^3
Pentane	72.15	1.8428	1.844	0.626	0.195	0.195	26.70	0.00	1345	45.64
Carbon disulfide	76.14	2.663	2.71	1.263	0.324	0.3295	27.90	0.05	534	23.89
Benzene	78.12	2.2534	2.283	0.8789	0.263	0.267	33.85	0.04	965	35.19
Hexane	86.18	1.891	1.891	0.66087	0.204	0.204	31.70	0.00	1488	51.68
Carbon tetrachloride	153.82	2.1324	2.24	1.5938	0.244	0.258	33.3	0.13	1094	38.31
Acetone	58.08	1.8464	22.62	0.79092	0.196	0.589	31.26	21.37	1212	29.08

[a] Λ_ε and Λ_n are functions describing the total solvent effect and its inductive constituent on the reactive field of the activator molecule, determined from its optical and static dielectric parameters; ΔH_v^0, I_{an}, I_{is}, and r_{str} are, respectively, the enthalpy of vaporization, anisotropic and isotropic solvation potentials, and structural radius of molecules in the condensed state [8].

Table 2. Anisotropic and isotropic constituents of the partial Helmholtz energy of solvation for model mixtures and pure liquids at 20°C under normal pressure[a]

$\Delta F_{is,max(1)/i}$	$\Delta F_{is,max(1)/i}$	$\Delta F_{is,max(2)/i}$	$\Delta F_{is,max(2)/i}$	$\Delta F_{an,max(3)/i}$	$\Delta F_{is,max(3)/i}$	$\Delta F_{an,max(4)/i}$	$\Delta F_{is,max(4)/i}$	$\Delta F_{an,max(5)/i}$	$\Delta F_{is,max(5)/i}$	$\Delta F_{an,max(6)/i}$	$\Delta F_{is,max(6)/i}$
0.00	**–48.51**	–0.01	–45.33	–0.01	–54.47	0.00	–53.22	–0.03	–54.42	–4.17	–46.15
0.00	–45.33	**–0.02**	**–51.72**	–0.01	–54.73	0.00	–48.68	–0.04	–53.17	–7.04	–44.09
0.00	–54.47	–0.01	–54.73	**–0.01**	**–62.86**	0.00	–59.26	–0.03	–62.15	–5.71	–52.26
0.00	–53.22	–0.01	–48.68	–0.01	–59.26	**0.00**	**–58.52**	–0.03	–59.38	–4.36	–50.49
0.00	–54.42	–0.01	–53.17	–0.01	–62.15	0.00	–59.38	**–0.03**	**–61.69**	–5.51	–52.04
0.00	–46.15	–0.02	–44.09	–0.02	–52.26	0.00	–50.49	–0.03	–52.04	**–12.59**	**–44.02**

[a] The data for self-associates are given in boldface; the central solvate molecule is indicated in parentheses in the subscript.

Table 3. Normalized partial constituents of the exchange energy in solvates and self-associates [10]

$\delta\Delta F_{(G\text{–}S)(1)(1\text{–}i)}/RT$	$\delta\Delta F_{(G\text{–}S)(2)(2\text{–}i)}/RT$	$\delta\Delta F_{(G\text{–}S)(3)(3\text{–}i)}/RT$	$\delta\Delta F_{(G\text{–}S)(4)(4\text{–}i)}/RT$	$\delta\Delta F_{(G\text{–}S)(5)(5\text{–}i)}/RT$	$\delta\Delta F_{(G\text{–}S)(6)(6\text{–}i)}/RT$
0.00	–1.96	–0.50	–0.12	–0.28	–0.92
–1.97	**0.00**	–1.05	–2.65	–1.44	–1.24
–0.50	–1.05	**0.00**	–0.59	–0.05	–0.73
–0.12	–2.64	–0.59	**0.00**	–0.29	–1.11
–0.29	–1.46	–0.06	–0.30	**0.00**	–0.66
–2.63	–4.12	–3.06	–2.90	–2.89	**0.00**

tion shell of the polar component. According to the φ_{bi} values, nonpolar molecules rank as follows: carbon tetrachloride > benzene > pentane > hexane > carbon disulfide.

The degree of self-association of nonpolar molecules is higher, and their competitive abilities with respect to acetone molecule form the series pentane > carbon disulfide > benzene > hexane ≈ carbon tetrachloride. The tendency to form emulsion is determined by the parameter m_{is}, and it changes in the series acetone/carbon disulfide > acetone/hexane ≈ acetone/benzene > acetone/pentane > acetone/carbon tetrachloride.

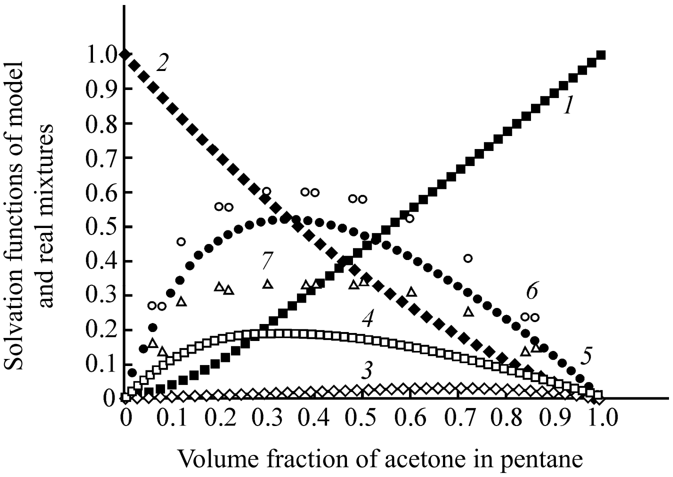

Fig. 1. Model solvation functions for acetone–pentane mixtures. Initial parameters: $\delta\Delta f_{(G-S)1(1-6)}/kT = -2.63$, $\delta\Delta f_{(G-S)6(6-1)}/kT = -0.92$; $(r_{str6})^3/(r_{str1})^3 = 29.08/45.64$; characteristic points on the solvation functions: $\varphi_{1i} = 0.993$, $\varphi_{6i} = 0.285$, $m_{1i} = 0.022$, $m_{6i} = 0.192$; $\varphi_{is} = 0.466$, $m_{is} = 0.397$.

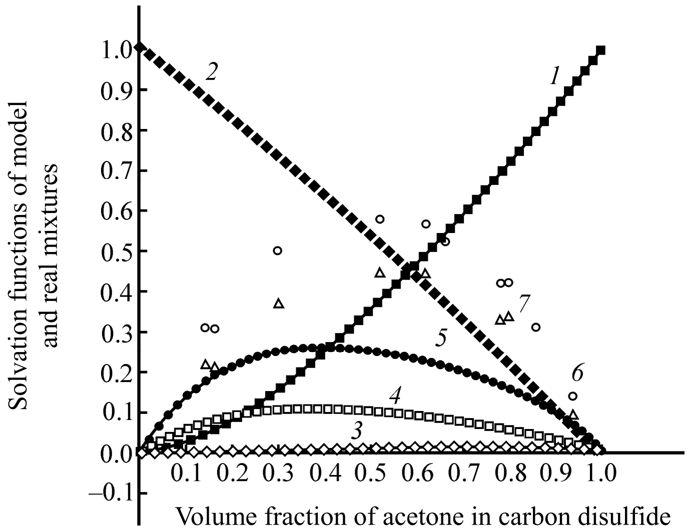

Fig. 2. Model solvation functions for acetone–carbon disulfide mixtures. Initial parameters: $\delta\Delta f_{(G-S)2(2-6)}/kT = -4.12$, $\delta\Delta_{(G-S)6(6-2)}/kT = -1.24$; $(r_{str6})^3/(r_{str2})^3 = 29.08/23.89$; characteristic parameters of solvation functions: $\varphi_{2i} = 0.984$, $\varphi_{6i} = 0.224$, $m_{2i} = 0.010$, $m_{6i} = 0.096$, $\varphi_{is} = 0.589$; $m_{is} = 0.449$.

Figure 1 illustrates the system acetone–pentane. Considerable difference of the volume-averaged compositions of solvation shells of acetone and pentane molecules from the composition of the mixture should be noted. Analysis of plots *1*–*5* shows that the mole fractions of self-associates in the model system are appreciably greater, and the mole fractions of mixed solvates are lower, than in the ideal solution (Fig. 1) [10]. The inversion points for the model system ($\varphi_{ai} = 0.993$, $\varphi_{bi} = 0.285$) are arranged asymmetrically with respect to the 1 : 1 (v/v) composition. This is also confirmed by the displaced isomeric point ($m_{is} = 0.397$). According to [10], m_{is} values range from 0 to 0.5, and $m_{is} = 0.25$ for an ideal solution. The lower limit is reached when the energy of solvation is much higher than the energy of self-association, and the upper limit corresponds to the opposite case. The function represented by curve *7* (molar change of the contribution of short-range molecular interactions to the energy of intermolecular interactions upon mixing shows an endothermic effect with its maximum at ~0.3 *RT* at a volume ratio φ_b of

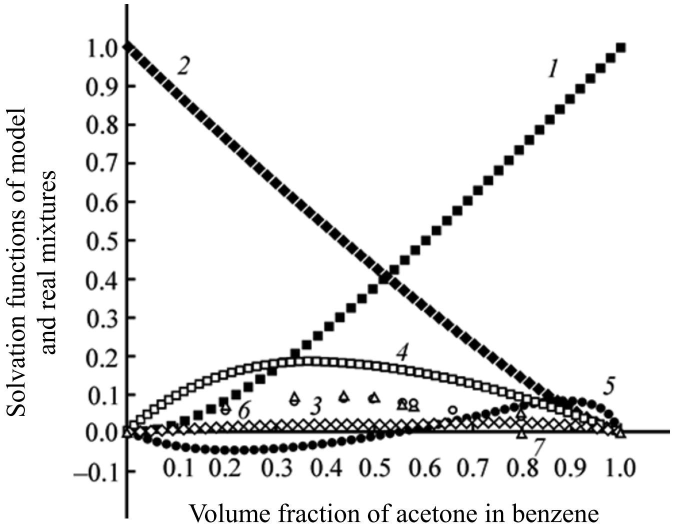

Fig. 3. Model solvation functions for acetone–benzene mixtures. Initial parameters: $\delta\Delta f_{(G-S)3(3-6)}/kT = -3.06$, $\delta\Delta f_{(G-S)\,6(6-3)}/kT = -0.73$; $(r_{str6})^3/(r_{str3})^3 = 29.08/35.19$; characteristic points on the solvation functions: $\varphi_{3i} = 0.955$, $\varphi_{6i} = 0.325$, $m_{3i} = 0.184$, $m_{6i} = 0.019$, $\varphi_{is} = 0.529$, $m_{is} = 0.403$.

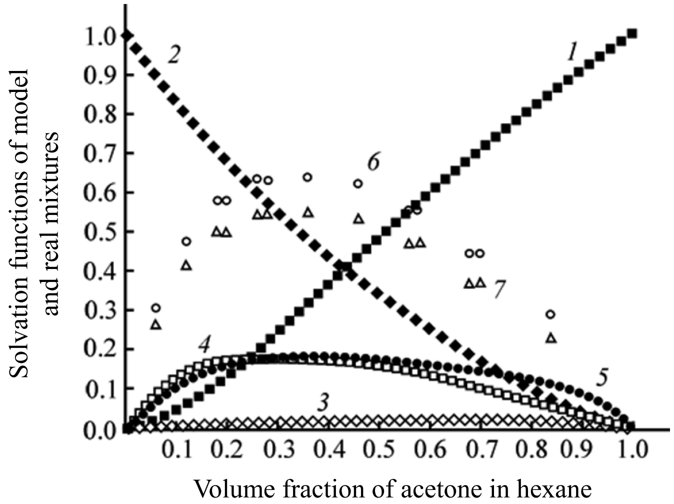

Fig. 4. Model solvation functions for acetone–hexane mixtures. Initial parameters: $\delta\Delta f_{(G-S)4(4-6)}/kT = -2.90$, $\delta\Delta f_{(G-S)6(6-4)}/kT = -1.11$; $(r_{str6})^3/(r_{str4})^3 = 29.08/51.68$; characteristic points on the solvation functions: $\varphi_{4i} = 0.948$, $\varphi_{6i} = 0.248$, $m_{4i} = 0.015$, $m_{6i} = 0.185$, $\varphi_{is} = 0.435$, $m_{is} = 0.405$.

~0.40 which is close to the equimolar composition ($\varphi_b \approx 0.39$). A low-boiling azeotrope was revealed for the real solution with an acetone volume fraction of $\varphi_b \approx 0.17$ [13]. The model system is expected to produce azeotrope at $\varphi_b \approx 0.06$. The difference is likely to be determined by the contribution of short-range molecular interactions (due to "disentanglement" of intertwined pentane chains by weak specific interactions [14]) to the total endothermic effect, which amounts to ~60%.

The model system acetone–carbon disulfide (Fig. 2) differs from all other examined systems in all initial parameters. The distance between the inversion points ($\varphi_{ai} = 0.984$, $\varphi_{bi} = 0.224$) is appreciably larger as compared to the acetone–pentane system due mainly to enhanced self-association of acetone (the difference between φ_a and φ_{bi} in an ideal solution is equal to zero [10]). The m_{is} value equal to 0.449 is almost twice as high as m_{is} for an ideal solution. This indicates appreciably increased tendency to self-association of acetone molecules, which attains its maximum value. The calculations suggest instability of the model system; therefore, emulsion may be formed in a real solution. The contribution of short-range molecular interactions to the endothermic effect of mixing for the

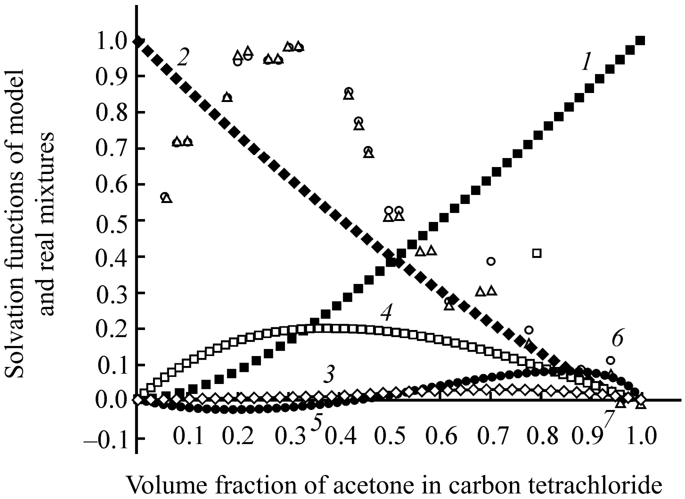

Fig. 5. Model solvation functions for acetone–carbon tetrachloride mixtures. Initial parameters: $\delta\Delta f_{(G-S)5(5-6)}/kT$ = –2.89, $\delta\Delta f_{(G-S)6(6-5)}/kT$ = –0.66; $(r_{str6})^3/(r_{str5})^3$ = 29.08/38.31; characteristic points on the solvation functions: φ_{5i} = 0.947, φ_{6i} = 0.341, m_{5i} = 0.020, m_{6i} = 0.203, φ_{is} = 0.516, m_{is} = 0.393.

acetone–carbon disulfide system amounts to more than 75% of its overall value, but their absolute values given in Figs. 1 and 2 coincide with each other. This means that the difference between the calculated and experimental parameters of the azeotrope should be greater than for the acetone–pentane system. In fact, acetone–carbon disulfide azeotrope contains 0.44 vol % of acetone [13] against $\varphi_b \approx 0.02$ for the model system.

Of particular interest is the model system acetone–benzene (Fig. 3). Here, the difference between the inversion points (φ_{ai} = 0.955, φ_{bi} = 0.325) is considerably smaller. Like the preceding system (acetone–carbon disulfide), the acetone–benzene system is characterized by a shift of the isomeric point toward fairly large mole fractions (m_{is} = 0.403). The function describing variation of the total solvation energy versus mixture composition (curve *5*) changes its sign in the range not exceeding 2*RT*. The sign of function *7* (energy effects of short-range molecular interactions) changes in a similar way. At an acetone concentration lower than 50 vol %, a weak entropy increase is observed due to decomposition of benzene–acetone associates, and it disappears at higher acetone concentration. Neither model system nor real solution tends to form azeotrope, though the difference in the energies of self-associates is smaller (Table 2).

The model acetone–hexane system shown in Fig. 4 is analogous to acetone–pentane mixtures (Fig. 1), but the change of the total solvation energy (curve *5*) is smaller. The distance between the inversion points (φ_{ai} = 0.948, φ_{bi} = 0.248) is insignificantly shorter as compared to the acetone–pentane system. Acetone–hexane mixtures are also characterized by a shift of the isomeric point (m_{is} = 0.405) toward higher mole fractions; however, the endothermic effect due to short-range molecular interactions is considerably greater. The reason is obvious. Taking into account that the carbon chain of hexane molecule is longer than pentane by one carbon atom, i.e., by about 20%, the endothermic effect arising from disentanglement of hexane molecules via specific intermolecular interactions should be clearly higher than in pentane. Possible formation of weak H-complexes by molecules of the components was demonstrated in [14] by IR spectroscopy. An essential difference between the initial components is that just acetone rather than hexane has the lowest solvation energy, and the difference in the solvation energies of the components changes its sign and decreases almost fivefold (Tables 1, 2). Therefore, the azeotropic composition should drift from low (as in the acetone–pentane system) to high acetone concentration. The volume fraction of acetone in the real azeotrope is φ_b = 0.55. The corresponding value for the model system is φ_b = 0.91. With account taken of the energy of short-range molecular interactions and their contribution to the heat of mixing, the observed shift of the azeotropic composition is consistent with those found for the systems considered above. It may be concluded that the formation of azeotrope and its composition are determined by the effects of both conventional intermolecular interactions and short-range molecular interactions on the energy of mixing and that their contributions make it possible to quantitatively estimate the proposed approach.

Figure 5 shows the model solvation functions for acetone–carbon tetrachloride mixtures. These mixtures are analogous to the acetone–benzene system in the initial anisotropic and isotropic solvation parameters. The range between the inversion points ($\varphi_{\mathrm{ai}} = 0.947$, $\varphi_{\mathrm{bi}} = 0.341$), which are also located asymmetrically with respect to the equivolume mixture, is the lowest among the examined binary mixtures. Self-association of the components decreases mainly due to acetone. The difference between the average solvation shell compositions of acetone and carbon tetrachloride molecules, on the one hand, and the mixture composition, on the other, remains considerable. The isomeric point, $m_{\mathrm{is}} = 0.393$, is characterized by the minimum value among the examined systems, but it also indicates considerably higher stability of self-associates as compared to mixed solvates. Variation of the total energy of solvation (within $1.5RT$) is described by a similar function (curve *5* in Figs. 3, 5). Acetone–carbon tetrachloride mixtures display the maximum experimental endothermic effect due to short-range molecular interactions. The observed dependence may be rationalized assuming decomposition of the ordered carbon tetrachloride structure as a result of formation of weak complexes comprising two acetone molecules and one carbon tetrachloride molecule. Acetone and carbon tetrachloride form an azeotrope. Analysis of the model solvation functions revealed azeotrope formation as well. The real acetone–carbon tetrachloride azeotrope contains 94 vol % of acetone ($\varphi_{\mathrm{b}} = 0.94$; the calculated value is 0.98). The contribution of short-range molecular interactions to the heat of mixing in the acetone–carbon tetrachloride system reaches its maximum value, but the calculated and experimental azeotrope compositions almost coincide with each other. This anomaly just confirms the general conclusion. In the near-azeotropic concentration range, the contribution of short-range molecular interaction to the energy of solvation is insignificant (Fig. 5, curves *6*, *7*); therefore, the experimental and calculated azeotrope parameters should be similar.

The proposed approach enables one to evaluate the contributions of short-range molecular interactions to the energy of solvation of real solutions, originating from both variation of the structure and associates of the initial components and formation of complexes. Theoretical analysis [10] and experimental data led me to draw a general conclusion that, unlike nonpolar solvent mixtures [11], there is no symmetry in the arrangement of the inversion points (φ_{ai} and φ_{bi}) with respect to the equivolume mixture ($\varphi_{\mathrm{b}} = 0.5$). This conclusion also follows from numerous data on ternary systems consisting of a binary solvent mixture and a luminescent label [8]. As shown in [8], the composition of luminophore solvate differs from the composition of the solution, and the difference is determined by the anisotropic potential of the luminophore molecule.

The results of the present study show that the new version of the continual parameter-free approach is applicable not only to determination of the absolute values of solvation energies [3] but also to quantitative evaluation of their differences. Plotting of model solvation functions made it possible to predict azeotrope formation for all the examined real systems [13]. The overall variations of the energy of short-range molecular interactions calculated on the basis of heats of mixing are consistent with the known physicochemical parameters.

The use of the parameter-free approach for the determination of variation of the energy of short-range molecular interactions in nonelectrolyte solutions, which is induced by structural reorganization of the components or formation of complexes with decomposition of associates, opens new prospects in predicting the direction of chemical processes and studying the structure and physicochemical properties of binary liquid nonelectrolyte mixtures.

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