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Anisotropic and Isotropic Components of Solvation Energy in Solutions. Model Thermodynamic Function of Extremely Dilute Solutions. Calculation Method and Applications

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Abstract—A model thermodynamic function describing the energy of solvation of organic substances in extremely dilute solutions has been proposed for the first time. Using this function, the chemical potentials of interaction of solute particles for extremely dilute solutions were calculated and compared with experimental data for about 180 systems. Solutions of polar and nonpolar associated and nonassociated substances in the liquid and gas phases were considered. The calculated and experimental partial enthalpies of solvation in cyclohexane for 40 organic compounds under normal conditions were compared. The feasibility of this approach for studying the microstructures and properties of extremely dilute solutions has been shown.
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Properties and regularities of the anisotropic and isotropic components of intermolecular interaction energies for approximately 190 associated and nonassociated single-component liquids [1] were considered earlier in detail. The approach in use can be applied for solutions. In particular, it allows one to calculate model thermodynamic functions of solutions, obtained on the assumption that the potentials of the anisotropic and isotropic intermolecular interactions, as well as the molar volumes of the components remain unchanged on solution formation. Differences between the calculated and real thermodynamic dependences forme the basis for qualitative and quantitative conclusions on processes that accompany solution formation.

According to the developed approach [1–6], the anisotropic and isotropic components of the partial Helmholtz solvation energy for N_A molecules of a solute in an extremely dilute solution ($\Delta F_{s,1}$) are given by Eqs. (1) and (2).

$$\Delta F_{an,1} = \Delta F_{an,1\,max} + (3/2)RT = -I_{an,1}\Lambda_{s,1} + (3/2)RT, \quad (1)$$

$$I_{an,1} \equiv (\varepsilon_{s,1} - n_1^2)(2\varepsilon_{s,1} + n_1^2)3RT/\varepsilon_{s,1}(n_1^2 + 2)^2,$$

$$\Lambda_{s,1} \equiv (n_1^2 + 2)(\varepsilon_s - 1)/3(2\varepsilon_s + n_1^2),$$

$$n_1^2 = (1 + 2\Phi_{n,1})/(1 - \Phi_{n,1}),$$

$$\Phi_{n,1} \equiv \alpha_1/r^3_{str,1}.$$

Here α_1 is the polarizability of solute molecules; $r^3_{str,1} = 4\pi V_{1m}/3N_A$, V_{1m} is the volume of 1 mol of the solute at the temperature of liquid solution or its partial volume in the gas phase (the subscript “1” relates exclusively to solute particles; the electro-optical parameters of the solvent are given without index); $I_{an,1}$ is the anisotropic solvation potential of the soluted; and $\Lambda_{s,1}$ is the corresponding solvation parameter of the medium.

$$\Delta F_{is,1} = \Delta F_{is,1\,max} + \delta\Delta F_{is(fl)}$$

$$= -(3/2)[(I_{is,1}I_{is})/(I_{is,1} + I_{is})]\Phi_{n,1}\Phi_n + \delta\Delta F_{is(fl)}. \quad (2)$$

Here I_{is} and $I_{is,1}$ are the conditional potentials of isotropic intermolecular interactions for solvent and solute molecules [1]; the product $\Phi_{n,1}\Phi_n$ represents the isotropic solvation parameter of the solution; and $\Phi_n \equiv n^2 - 1)/(n^2 + 1)$.

The first term in Eqs. (1) and (2) is equal to the maximum solvation energy in arbitrarily selected N_A solvates per one mole (further designated as $\Delta F_{an,1\,max}$ and $\Delta F_{is,1\,max}$, and their sum is designated as $\Delta F_{s,1\,max}$ [1]). The second term includes the mean-square contribution of fluctuations to the solvation energy in noninteracting N_A solvates. The values of $I_{is,1}$ and I_{is} are taken from [1] or calculated by the method described in [3].

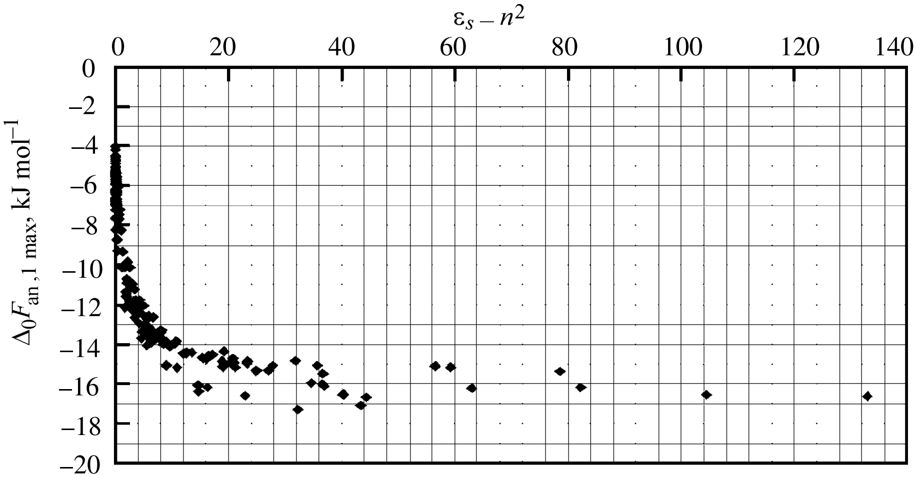

Fig. 1. Correlation between the anisotropic component of the partial Helmholtz solvation energy of substance 1 in solutions ($\Delta_0 F_{an,1\,max}$) and the anisotropic solvation function of solvents $\varepsilon_s - n^2$ at $I_{an,1}$ 25 kJ mol^{-1}.

The anisotropic and isotropic components of the works of cutting-off the interaction (equal to corresponding solvation energies but taken with the opposite sign) between arbitrarily selected particles (molecules and associates) of a solvent containing a total of N_A molecules and their environment in an extremely large liquid volume (at constant T and V) are designated as $-\Delta F_s$, $-\Delta F_{an}$, and $-\Delta F_{is}$, respectively.

According to [1], we have expressions (3) and (4).

$$-\Delta F_{an} = I_{an}\Lambda_s - (3/2)RT$$
$$= (\varepsilon_s - n^2)(\varepsilon_s - 1)RT/\varepsilon_s(n^2 + 2) - (3/2)RT, \quad (3)$$
$$-\Delta F_{is} = (3/4)I_{is}\Phi_n^2 - \delta\Delta F_{is(fl)}. \quad (4)$$

Correspondingly, $\Delta F_{s,max} = \Delta F_{an,max} + \Delta F_{is,max} = -I_{an}\Lambda_s - (3/4)I_{is}\Phi_n^2$.

It is necessary to emphasize that the functions $\Delta F_{an,1\,max}$, $\Delta F_{is,1\,max}$ and $-\Delta F_{an,max}$, $-\Delta F_{is,max}$ have different dependences on the solvation parameters of the medium. Let us transform Eqs. (2) and (4) to another form.

$$\Delta F_{is,1\,max} = -(3/2)[(I_{is,1})/(I_{is,1} + I_{is})]\Phi_{n,1}I_{is}\Phi_n, \quad (2')$$
$$-\Delta F_{is,max} = (3/4)\Phi_n I_{is}\Phi_n. \quad (4')$$

Isotropic intermolecular interactions are suggested to describe by the product $I_{is}\Phi_n$ (generalized parameter of isotropic solvation of the medium). This substitution allows us not only to group data, but also to reveal differences in the patterns of the $\Delta F_{is,1\,max}$ and $-\Delta F_{is,max}$ dependences, which describe the energies of solvation and cavity formation in the solution, due to isotropic intermolecular interactions.

The dependences of $\Delta F_{an,1\,max}$ on ($\varepsilon_s - n^2$) and of $\Delta F_{is,1\,max}$ on $I_{is}\Phi_n$ have a similar exponential shape described by Eq. (5).

$$y_i = A_i[1 - \exp(-x_i/a_i)], \quad (5)$$
$$i \equiv an,\ is.$$

Here y_i stands for $\Delta F_{an,1\,max}$ or $\Delta F_{is,1\,max}$; x_i is the corresponding solvation parameter of the solvent: ($\varepsilon_s - n^2$) or $I_{is}\Phi_n$; and A_i is a parameter equal to a limiting possible y_i value attained at $x_i \to \infty$. In the case of anisotropic intermolecular interactions, $A_{an} = -I_{an,1}$; for isotropic intermolecular interactions, $A_{is} = -(3/4)I_{is,1}\Phi_{n,1}$; the value of A_{is} was obtained under the condition: $I_{is} >> I_{is,1}$ and $\Phi_{n,max} \sim 0.5$; and a_i is a parameter equal to the value of x_i, at which $y_i = 0.632A_i$.

Figures 1 and 2 present the characteristic dependences for solutions of dyes in a series of about 200 solvents. As shown in Fig. 1, the dependence of $\Delta F_{an,1\,max}$ on ($\varepsilon_s - n^2$) rapidly tends to saturation and reaches the value $0.632A_{an}$ at a_{an} ~16 [the parameter ($\varepsilon_s - n^2$) is varied from 0 to 140]. For the dependence of $\Delta F_{is,1\,max}$ on $I_{is}\Phi_n$ (Fig. 2) we found the value A_{is} ~2600 kJ mol^{-1} (the parameter $I_{is}\Phi_n$ is varied from 0 to 1000). Therefore, this function slowly tends to saturation and, when the generalized parameter $I_{is}\Phi_n$ is varied in a fairly narrow range, is roughly linear. The tendency of the dependences to separate (Figs. 2–4) requires special consideration, which is beyond the scope of the present paper.

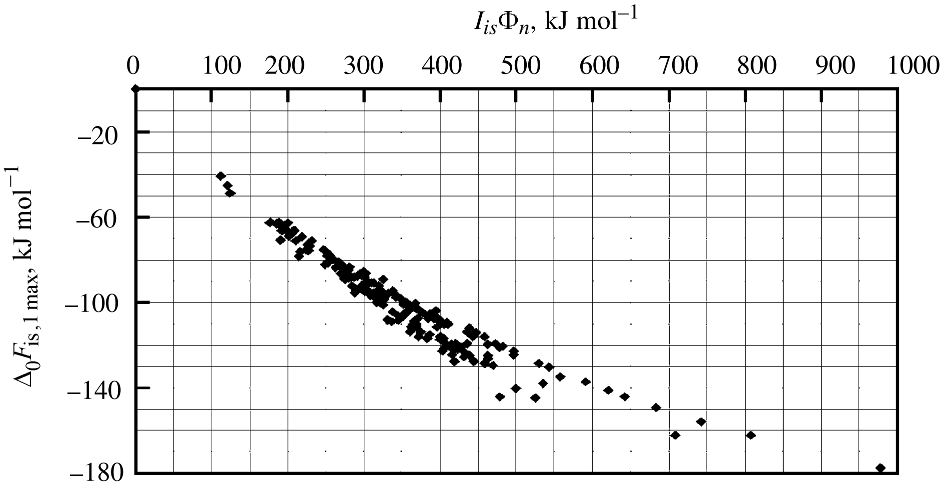

Fig. 2. Correlation between the isotropic component of the partial Helmholtz solvation energy of substance 1 ($I_{\text{is},1}$ 2500 kJ mol^{-1}, $\Phi_{n,1}$ 0.3) in solutions ($\Delta_0F_{\text{is,1 max}}$) and the generalized isotropic solvation parameter of solvents $I_{\text{is}}\Phi_n$.

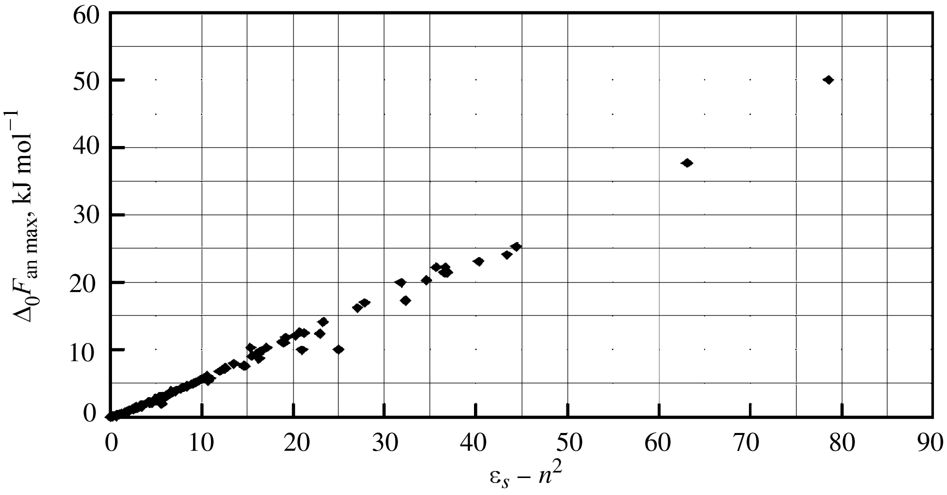

Fig. 3. Correlation between the anisotropic component of the Helmholtz desolvation energy of solvent molecules ($\Delta_0F_{\text{an max}}$) and the anisotropic solvation function ($\varepsilon_s - n^2$).

In pure liquids, the character of the $\Delta F_{\text{an max}}$ and $\Delta F_{\text{is max}}$ functions essentially changes. The $F_{\text{an max}}$ dependence on ($\varepsilon_s - n^2$), as well as the dependence $\Delta F_{\text{is max}}$ on $I_{\text{is}}\Phi_n$ are linear in the series of solvents (Figs. 3 and 4); this is also proved also by correlations (6) and (7).

$$-\Delta F_{\text{an max}} = (0.65 \pm 0.01)(\varepsilon_s - n^2) + (-0.15 \pm 0.10), \quad (6)$$
$$N = 189,\ \Delta S = 1.2\ \text{kJ mol}^{-1},\ R = 0.992. \quad ,$$

$$-\Delta F_{\text{is max}} = (0.21 \pm 0.01) I_{\text{is}}\Phi_n + (-4.8 \pm 2.0), \quad (7)$$
$$N = 189,\ \Delta S = 8.7\ \text{kJ mol}^{-1},\ R = 0.945.$$

Here N is the number of solvents, ΔS is the standard deviation, and R is the correlation coefficient.

Theoretical analysis of dependences (1), (2) and (6), (7), that characterize the energies of particle solvation and cavity formation, respectively, allows some important conclusions at the initial stage. The energy of transfer of a particle from vapor into dilute solution (with preliminary cavity formation) should be determined by the solvent functions n^2 and Φ_n (determining its molar refraction) and only slightly depend on ε_s. In fact, $\Delta F_{\text{an,1 max}}$ reaches saturation at the ε_s of about 20, whereas $-\Delta F_{\text{an max}}$ continues to grow linearly, compensating the effect of the anisotropic solvation energy. On the contrary, the $\Delta F_{\text{is,1 max}}$ value for dyes usually does not reach saturation even if the generalized parameter $I_{\text{is}}\Phi_n$ is widely varied. It remains roughly linear for dye molecules ($I_{\text{is}}\Phi_n$ is

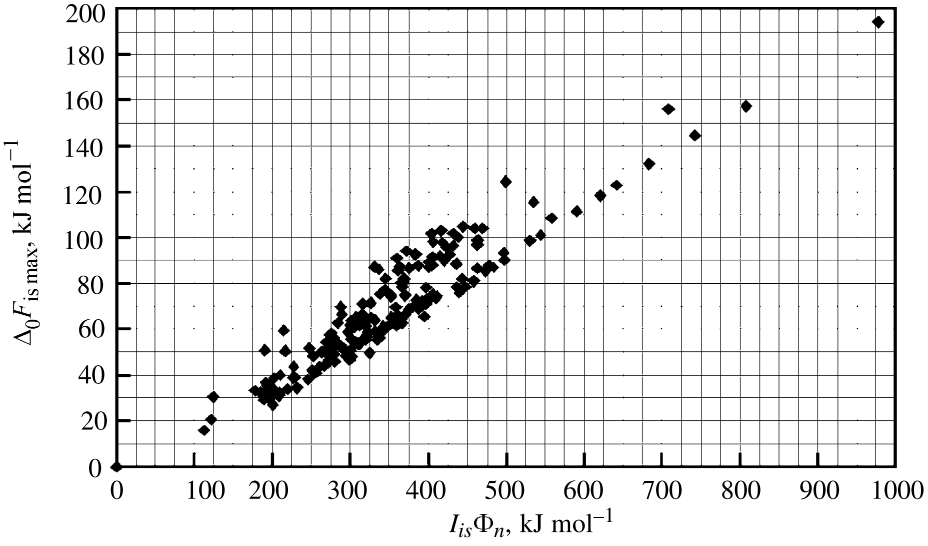

Fig. 4. Correlation between the isotropic components of the Helmholtz desolvation energy of randomly chosen molecules of a substance ($\Delta_0 F_{\mathrm{an\,max}}$) and its generalized isotropic solvation parameter ($\Phi_n I_{\mathrm{is}}$).

varied from 200 to 600 kJ mol^{-1}) with a slope noticeably larger than the slope for $\Delta F_{\mathrm{is\,max}}$ for pure liquids. Furthermore, as the molecular weight of the solute increases, the ratio between the anisotropic and isotropic contributions to the solvation energy changes in favor of the latter contribution. As shown earlier [3], the variations of the internal energy of a dilute solution, caused by anisotropic solvation of solute molecules, are determined by Eq. (8).

$$\Delta U_{\mathrm{an},1} = -I_{\mathrm{an},1}[\Lambda_{\mathrm{s},1}$$
$$+ (n_1^2 + 2)^2(2\varepsilon_{\mathrm{s}} + n^2)\varepsilon_{\mathrm{s}}(\varepsilon_{\mathrm{s}} - n^2)/(2\varepsilon_{\mathrm{s}} + n_1^2)^2(2\varepsilon_{\mathrm{s}}^2 + n^4)]. \quad (8)$$

This expression also predicts an almost linear correlation of $\Delta U_{\mathrm{an},1}$ with the electron polarizability parameter n_1^2 of the solute and a weak nonlinear (with the saturation effect) dependence on the ε_{s} of the solvent. These regularities of solvation thermochemistry were empirically established earlier and studied in detail on a vast experimental material [7]. Note that the energies of cavity formation in the ground and excited states of a molecule differ only slightly. Therefore, the dependence of the shift of the spectrum of a substance on the ε_{s} of the solvent (caused mainly by the difference in the solvation energies but not by the difference in the energies of cavity formation) becomes rather essential [2].

To check the feasibility of the proposed method, in this paper we compared the chemical potentials of molecular interaction ($\Delta\mu_1$) for a number of organic and inorganic substances in extremely dilute solutions (obtained on the basis of the Henry coefficients in the monograph [8]) with their values calculated using the model thermodynamic function of solutions. The calculated chemical potentials of molecular interactions, designated as $\Delta_0 F_{1(\mathrm{s-v})}$, were equated to the changes of the Helmholtz energy of extremely dilute solutions, produced by cuttingoff intermolecular interactions between N_{A} molecules of the solute and the solvent, with subsequent cavity closure, on the additional condition that the potentials $I_{\mathrm{is},1}$, I_{is} and $I_{\mathrm{an},1}$, I_{an} remain unchanged. The calculation of $\Delta_0 F_{1(\mathrm{s-v})}$ was carried out by means of postulated relation (9). In what follows $\Delta\mu_1$ are named in the abbreviated form as chemical potentials of intermolecular interactions, and $\Delta_0 F_{1(\mathrm{s-v})}$, as the work of transfer of N_{A} molecules of substance 1 from solution to vapor.

$$\Delta_0 F_{1(\mathrm{s-v})} = -\Delta F_{\mathrm{s},1\,\mathrm{max}} + (1/2)\Delta F_{\mathrm{s\,max}}. \quad (9)$$

Here the second term includes the maximum energy of solvent cavity closure. As the first approximation we did not take into account the works against external pressure forces originating from the difference in the volumes occupied by solute and solvent molecules and also the total contribution of fluctuation effects to the $\Delta_0 F_{1(\mathrm{s-v})}$ value. In total, under nearly normal conditions, these effects contribute fairly little to the $\Delta_0 F_{1(\mathrm{s-v})}$ value (within experimental error) and only slightly affect the character of the regularities under consideration. On the basis of relations (1)–(4) and accepted assumptions we can present expression (9) in the final form (10).

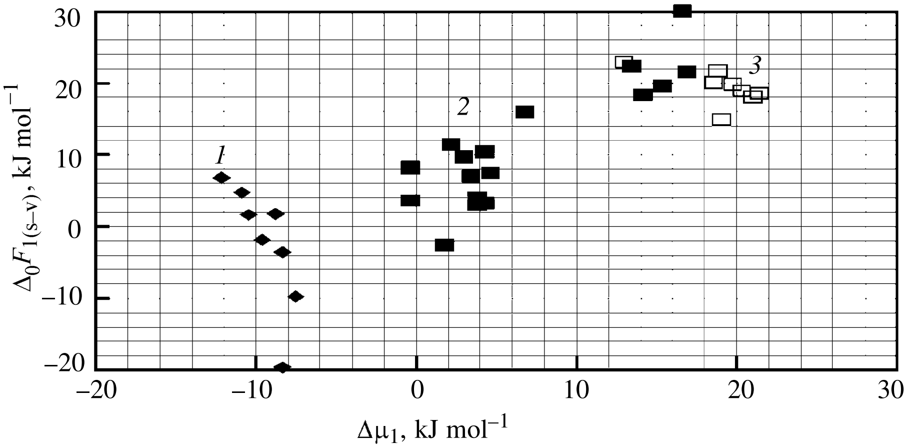

Fig. 5. Correlation of the calculated works of transfer of 1 mol of organic substances from an extremely dilute aqueous solution (I_{an} 81.4 kJ mol^{-1}, I_{is} 1021 kJ mol^{-1}, Λ_s 0.614, and Φ_n 0.206) into saturated vapor with their chemical potentials of intermolecular interactions. (*1*) Alkanes, (*2*) nonassociated substances, and (*3*) associated substances. Methane –8.37, –19.6; ethane –7.5, –9.7; methanol 21.4, 18.7; propane –8.4, –8.0; ethanol 21.0, 18.1; *n*-butane –8.8, –6.3; nitromethane 16.9, 21.6; propan-1-ol 20.3, 18.9; *n*-pentane –9.6, –1.9; butan-1-ol 19.7, 19.9; *tert*-butanol 19.0, 14.9; nitroethane 15.3, 19.6; carbon disulfide 1.7, –2.5; benzene 3.8, 4.0; dichloromethane 3.8, 3.1; *n*-hexane –10.5, 1.7; pentan-1-ol 18.5, 20.1; 1-nitropropane 14.1, 18.4; toluene 3.4, 7.1; *n*-heptane –10.9, 4.7; hexan-1-ol 18.8, 21.8; *o*-xylene 4.2, 10.5; ethylbenzene 2.9, 9.7; chlorobenzene 4.6, 7.5; *n*-octane –12.1, 6.8; chloroform 4.2, 3.3; isopropylbenzene 2.1, 11.5; nitrobenzene 16.5, 30.0; octan-1-ol 12.9, 22.9; tetraline 6.7, 16.0; tetrachloromethane –0.42, 3.6; tetrachloroethylene –0.42, 8.2; and diphenylmethane 13.4, 22.3 ($\Delta_0F_{1(s-v)}$ values are printed bold).

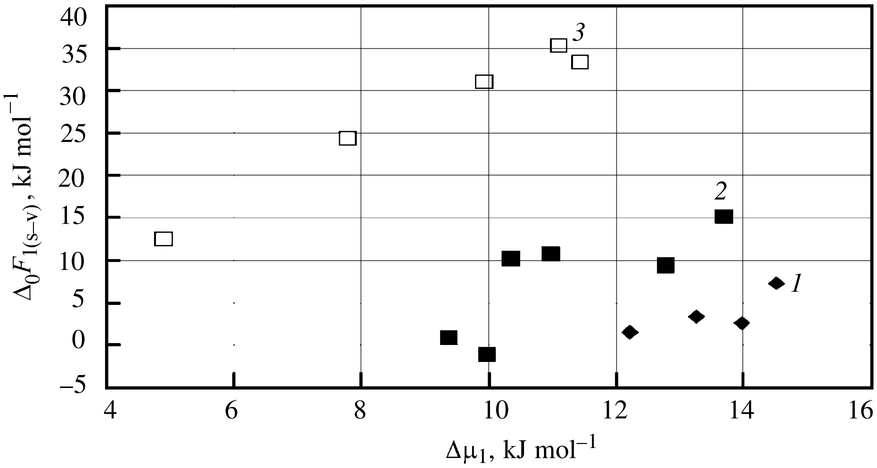

Fig. 6. Correlation of the calculated works of transfer of 1 mol of organic substances from an extremely dilute solution in *n*-hexadecane (I_{an} 0 kJ mol^{-1}, I_{is} 3112 kJ mol^{-1}, Λ_s 0.231, Φ_n 0.261) into saturated vapor with their chemical potentials of intermolecular interactions. (*1*) Alkanes; (*2*) polar nonassociated substances; and (*3*) alcohols. Methanol 4.9, 12.6; ethanol 7.8, 24.5; propan-1-ol 11.4, 33.5; propan-2-ol 9.9, 31.1; *tert*-butanol 12.8, 9.5; propanal 10.0, –0.95; acetone 9.4, 0.96; cyclopentane 14.0, 2.6; butan-2-ol 12.8, 9.5; *n*-pentane 12.2, 1.6; 3-methylpentane; 14.3, 7.3; 2,2-dimethylbutane 13.3, 3.4; ethyl formate 10.3, 10.3; methyl acetate 11.0, 11.0; and ethyl acetate 13.7, 15.3 ($\Delta_0F_{1(s-v)}$ values are printed bold).

$$\Delta_0F_{1(s-v)} = I_{an,1}\Lambda_{s,1} + (3/2)[(I_{is,1}I_{is})/(I_{is,1} + I_{is})]\Phi_{n,1}\Phi_n - (1/2)I_{an}\Lambda_s - (3/8)I_{is}\Phi_n^2. \qquad (10)$$

In the absence of experimental values of $I_{an,1}$, it is admissible to use the approximation $I_{an,1} = m_{0,1}^2/r_{str,1}^3$, where $m_{0,1}$ is the gas-phase dipole moment of the solute molecule.

The dependences of $\Delta_0F_{1(s-v)}$ on $\Delta\mu_1$ for series of extremely dilute solutions at room temperature (20–25°C) are compared in Figs. 5 and 6 and in Tables 1–4. Corresponding correlations (11) are given in addition.

$$\Delta\mu_1 = b\Lambda_0F_{1(s-v)} + a, \qquad (11)$$

(*b* and *a* are empirical parameters).

Table 1. Correlation of the calculated works (kJ mol^{-1}) of transfer of 1 mol of water from an extremely diluted solution in an organic solvent into saturated vapor with their chemical potentials of intermolecular particle interactions

Solvents	$\Delta\mu_1$ (experiment)	$-\Delta_0F_{1(s-v)}$ (calculation)			
		Hydrocarbons	Chloroalkanes	Nitroalkanes, acetonitrile	Pyridine, carbon disulfide, diethyl ether, acetone
Acetonitrile	18.6			53.5	
Acetone	18.3				56.6
Nitromethane	17.0			53.3	
Pentane	2.9	30.8			
2-Methylbutane	2.3	31.2			
Diethyl ether	17.0				47.1
Nitroethane	14.9			53.5	
Carbon disulfide	4.2				37.5
Benzene	7.6	34.4			
Pyridine	20.8				54.3
Cyclohexane	3.0	31.9			
Dichloromethane	11.8		55.2		
Hexane	3.9	29.9			
1-Nitropropane	13.3			53.0	
Toluene	7.3	34.0			
1,2-Dichloroethane	10.9		54.7		
Heptane	3.8	28.5			
Chlorobenzene	7.3	49.0			
Octane	3.6	26.8			
Isooctane	1.3	29.2			
Chloroform	9.5		48.2		
Nitrobenzene	9.5	50.5			
Trichloroethylene	7.3		41.8		
Tetrachloromethane	3.6		34.1		
Tetrachloroethylene	5.0		32.5		
Pentachloroethane	7.3		38.4		

The latter correlation shows the changes in the model system with the components preserving properties of pure liquids, which should be made to obtain a true solution.

Let us consider a procedure allowing us to reveal the chemical sense of the resulting correlation constants. Let us assume that the dependences of $\Delta\mu_1$ and $\Delta_0F_{1(s-v)}$ on a defining solvation parameter (Θ) are roughly linear [Eqs. (12)].

$$\Delta\mu_1 \approx b_\mu\Theta + a_\mu,$$
$$\Delta_0F_{1(s-v)} \approx b_F\Theta + a_F. \quad (12)$$

The energy of cavity closure contributes most to the a_μ and a_F values. Combining these relations and reducing the parameter Θ, we obtain dependence (13) whose fitting to experimental correlation (11) give us relations (14) and (15).

$$\Delta\mu_1 \approx (b_\mu/b_F)\Delta_0F_{1(s-v)} + [a_\mu - (b_\mu/b_F)a_F], \quad (13)$$

$$b = b_\mu/b_F, \quad (14)$$

$$a = a_\mu - ba_F. \quad (15)$$

Analysis of the constants obtained from correlation (11) with account for relations (13)–(15) allows some preliminary conclusions on processes occurring on the solvate level and also in the bulk solution on its formation. Aside from the zero variant, when the solutes and solvent preserve their initial potentials of solvation in solution, the following limiting cases are possible.

(1) The $I_{an,1}$ and $I_{is,1}$ potentials in solution remain unchanged, but solvates activated by solute particles are situated closely to the solution surface. Under these conditions, we can choose two variants.

(1a) Activated solvates are in the surface layer. The following correlation constants should be expected for it: $b < 1$ and $a \sim 0$. In fact, the transfer of the activated solvate from the bulk solution in its surface layer will proportionally reduce both a_μ and b_μ. As a result, these effects will compensate each other.

(1b) Solute molecules pass immediately to a surface of solution as the layers begin to separate. In this case, various inequalities can be obeyed: $b < 1$, but $a >> 0$. In this case, a correlation should be observed between $\Delta\mu_1$ and $\Delta H_{v(1)}$, because $\Delta F_{s,1(s-v)} = 0.5\Delta F_{s,1} \sim \Delta H_{v(\mathbf{1})}$, where $\Delta F_{s,1}$ is the work of cutting-off the interaction between molecules of solute 1 in the form of the pure liquid in N_A solvates.

(2) The $I_{an,1}$ and $I_{is,1}$ potentials vary, but the activated solvate is in the bulk solution. The limiting variants are also possible here.

(2a) The $I_{an,1}$ and $I_{is,1}$ potentials noticeably decrease, for example, when associates of solute particles are destructed, which is accompanied by decrease in the b_μ value. This, in turn, should lead to the following result: $b < 1$, $a << 0$, as $a_{\mu 1} \sim a_F \sim$ "$-\Delta H_v$" ("$-\Delta H_v$" is the average heat of cavity closure in a series of solvents with the same solute or analogous heat with the same solvent in a series of solutes).

(2b) The $I_{an,1}$ and $I_{is,1}$ potentials noticeably increase, for example, upon on complex formation; then: $b > 1$ and $>> 0$. It is natural that apart from the limiting variants intermediate cases are also possible.

Figure 1 presents data for extremely dilute solutions of organic substances in water. For all these systems, a common correlation (16) close to variant 1a is observed.

$$\Delta\mu_1 = (0.85 \pm 0.10)\Delta_0 F_{s,1(s\text{-}v)} + (-2.7 \pm 1.5), \qquad (16)$$

$$N = 33;\ \Delta S = 6.1\ \text{kJ mol}^{-1};\ R = 0.83.$$

As seen from Fig. 5, alkanes and normal alcohols form separate groups with opposite signs of the slope b. Furthermore, when an CH_2 group is added to linear hydrocarbon radical, $\Delta_0 F_{1(s-v)}$ changes much stronger than $\Delta\mu_1$. Such differences provide evidence *s* howing that alkane molecules are arranged directly on the water surface. In this case, the calculated difference of the $\Delta_0 F_{1(s-v)}$ values in going from methane to octane will change from ~26 to ~13 kJ mol^{-1}. However, even this calculated value is essentially larger *r* than the difference in $\Delta\mu_1$ ~2.5 kJ mol^{-1}. Such underestimated values of the chemical potentials of intermolecular interactions are possible if the structures of alkane molecules in the liquid state and in the aqueous solution essentially differ from each other. Independent

Table 2. Correlation of the calculated works (kJ mol^{-1}) of transfer of 1 mol of an organic substance from extremely dilute solutions in ethanol into saturated vapor with their chemical potentials of intermolecular particle interactions

Substances	μ_1 (experiment)	$-\Delta_0 F_{1(s-v)}$ (calculation)
Ammonia	26.5	15.0
Carbon disulfide	25.9	8.8
Benzene	32.6	21.4
Chlorobenzene	42.3	25.1
Chloroform	34.9	20.4
Tetrachloromethane	32.0	22.0

Table 3. Correlation of the calculated works (kJ mol^{-1}) of transfer of 1 mol of an organic substance from extremely dilute solutions in acetone into saturated vapor with their chemical potentials of intermolecular particle interactions

Substances	μ_1 (experiment)	$-\Delta_0 F_{1(s-v)}$ (calculation)
Methane	–3.1	–12.5
Acetylene	7.6	–7.3
Ethylene	3.2	–1.3
Ethane	2.9	0.5
Carbon disulfide	13.1	15.3
Benzene	18.9	24.0
Chlorobenzene	23.7	27.5
Chloroform	20.2	23.0

Table 4. Correlation of the calculated works (kJ mol^{-1}) of transfer of 1 mol of an organic substance from extremely dilute solutions in benzene into saturated vapor with their chemical potentials of intermolecular particle interactions

Substances	μ_1 (experiment)	$-\Delta_0 F_{1(s-v)}$ (calculation)	
Methane	–1.4	–10.5	
Acetylene	3.9	–3.9	
Ethylene	3.1	0.0	
Ethane	3.5	1.9	
Methanol	10.8		31.2
Ethanol	13.3		35.9
1-Propanol	16.2		39.8
1-Butanol	19.0		42.9
1-Chloropropane	15.9	25.7	
1-Chlorobutane	18.8	30.2	

evidence for this conclusion comes from the fact that the partial molar volumes of octane in water (141 $cm^3\,mol^{-1}$) and in the liquid state (163.6 $cm^3\,mol^{-1}$) are close to each other under normal conditions. The partial molar volume of octane in water is close to the molar volume of hexamethylethane in the liquid state (139 $cm^3\,mol^{-1}$). However, the decrease in $r^3_{str,1}$ should be accompanied by the increase in $\Phi_{n,1}$ from 0.241 to ~0.279. Thus, the difference between the patterns of the $\Delta_0 F_{1(s-v)}$ and $\Delta\mu_1$ functions in the series of normal alkanes will more and more increase. This inconsistency can be eliminated assuming that the molecules of normal alkanes in water can roll up. In this case, the number of external atomic interactions between alkane and water molecules decreases. Statistical analysis gave indirect evidence for this assumption. When we excluded pentane, hexane, and octane, and also the corresponding alcohol series were excluded from consideration, we obtained correlation (16') with noticeably better characteristics.

$$\Delta\mu_1 = (0.76 \pm 0.09)\Delta_0 F_{1(s-v)} + (-0.4 \pm 1.3), \quad (16')$$
$$N = 26,\ \Delta S = 4.9\ \mathrm{kJ\,mol^{-1}},\ R = 0.88.$$

Table 1 presents data for a series of solutions of water in organic solvents. A satisfactory common correlation (17) is observed.

$$\Delta\mu_1 = (0.48 \pm 0.05)\Delta_0 F_{1(s-v)} + (-11.4 \pm 2.3), \quad (17)$$
$$N = 26,\ \Delta S = 2.85\ \mathrm{kJ\,mol^{-1}},\ R = 0.85.$$

The resulting values of the constants *b* and *a* in correlation (17) correspond to case 2a. Correlation (17) was improved without changing its character after exclusion of the solutions in pyridine and diethyl ether whose molecules are capable of interacting actively with water molecules to destroy its associates and to form complexes.

$$\Delta\mu_1 = (0.44 \pm 0.05)\Delta_0 F_{1(s-v)} + (-10.1 \pm 2.0), \quad (18)$$
$$N = 24,\ \Delta S = 2.35\ \mathrm{kJ\,mol^{-1}},\ R = 0.88.$$

Analysis of relation (10) shows that in cases where $I_{an,1} > I_{an}$ and $I_{is,1} < I_{is}$ the solvation parameter of anisotropic intermolecular interactions Λ_s determines changes in $\Delta_0 F_{1(s-v)}$ from solvent to solvent. Statistical analysis gave expected correlations not only between $\Delta_0 F_{1(s-v)}$ and Λ_s, but also between $\Delta\mu_1$ and Λ_s (19, 20).

$$\Delta_0 F_{1(s-v)} = (64.8 \pm 3.3)\Lambda_s + (17.3 \pm 1.4), \quad (19)$$
$$N = 26,\ \Delta S = 2.6,\ R = 0.97.$$

$$\Delta\mu_1 = (32.2 \pm 3.7)\Lambda_s + (-3.3 \pm 1.5), \quad (20)$$
$$N = 26,\ \Delta S = 2.9\ \mathrm{kJ\,mol^{-1}},\ R = 0.91.$$

For solutions in ethanol (Table 2), $\Delta\mu_1$ and $\Delta_0 F_{1(s-v)}$, too, satisfactorily correlate with each other [Eq. (21)], and this correlation corresponds to variant 1a.

$$\Delta\mu_1 = (0.44 \pm 0.12)\Delta_0 F_{1(s-v)} + (7.9 \pm 2.3), \quad (21)$$
$$N = 6,\ \Delta S = 1.5\ \mathrm{kJ\,mol^{-1}},\ R = 0.985.$$

After exclusion of the solution of carbon disulfide in alcohol we obtained a qualitatively better correlation (21') which, too, corresponding to case 1a.

$$\Delta\mu_1 = (0.7 \pm 0.2)\Delta_0 F_{1(s-v)} + (2.3 \pm 3.6), \quad (21')$$
$$N = 5,\ \Delta S = 1.3\ \mathrm{kJ\,mol^{-1}},\ R = 0.997.$$

Correlations (16') and (21') for extremely dilute water and ethanol solutions with close chemical properties are also analogous.

Table 3 relates to extremely dilute solutions of organic substances in acetone. In calculating $\Delta_0 F_{1(s-v)}$ for lower hydrocarbons, the $\Phi_{n,1}$ values were calculated by the Lorentz–Lorenz formula using the mean *r* electronic polarizabilities and partial volumes of these compounds in acetone [2]. Correlation (22), intermediate in its form between variants 1a and 1b, was obtained for all acetone solutions.

$$\Delta\mu_1 = (0.59 \pm 0.07)\Delta_0 F_{1(s-v)} + (5.4 \pm 1.1), \quad (22)$$
$$N = 8,\ \Delta S = 2.75\ \mathrm{kJ\,mol^{-1}},\ R = 0.92.$$

Having excluded solutions of methane and acetylene in acetone, we obtained dependence (22') which better fits variant 1a.

$$\Delta\mu_1 = (0.71 \pm 0.03)\Delta_0 F_{1(s-v)} + (3.2 \pm 0.6), \quad (22')$$
$$N = 6,\ \Delta S = 0.95\ \mathrm{kJ\,mol^{-1}},\ R = 0.99.$$

As seen from Table 4 in the case solutions in benzene associated and nonassociated substances form separate groups [correlations (23) and (24), respectively].

$$\Delta\mu_1 = (0.7 \pm 0.05)\Delta_0 F_{1(s-v)} + (-11.3 \pm 1.8), \quad (23)$$
$$N = 4,\ \Delta S = 0.4\ \mathrm{kJ\,mol^{-1}},\ R = 0.99.$$

$$\Delta\mu_1 = (0.48 \pm 0.03)\Delta_0 F_{1(s-v)} + (3.8 \pm 0.5), \quad (24)$$
$$N = 6,\ \Delta S = 1.1\ \mathrm{kJ\,mol^{-1}},\ R = 0.99.$$

Correlation (23) for solutions of alcohols in benzene corresponds to variant 2a, and correlation (24) for nonassociated substances is closest to variant 1b. In fact, a well-pronounced correlation (25) between $\Delta\mu_1$ and the heat of vaporization of the solutes is observed for the solutions under consideration.

$$\Delta\mu_1 = (0.75 \pm 0.05)H_{v(1)} + (-6.7 \pm 0.9), \quad (25)$$
$$N = 6,\ \Delta S = 1.1\ \text{kJ mol}^{-1},\ R = 0.99.$$

Comparison of the dependences under study for extremely dilute solutions of substances in benzene and in hexadecane is of a special interest. By contrast to benzene, hexadecane has a much higher I_{is} than the solutes. This suggests that $\Delta\mu_1$ depends on the isotropic solvation parameters of the latter. For alcohol solutions, a linear correlation between $\Delta\mu_1$ and $I_{is,1}$ is observed with a correlation coefficient R of 0.96 and a maximum deviation of 1.5 kJ mol^{-1}.

The dependences presented in Fig. 6 show that the solutes form several groups, like in Table 4.

Correlation for associated substances:

$$\Delta\mu_1 = (0.29 \pm 0.02)\Delta_0 F_{1(s-v)} + (1.1 \pm 0.6), \quad (26)$$
$$N = 5,\ \Delta S = 0.4\ \text{kJ mol}^{-1},\ R = 0.996.$$

In the case of nonassociated substances, separation into subgroups is evident: (1) alkanes and (2) esters, aldehydes, and ketones.

Correlation for alkanes:

$$\Delta\mu_1 = (0.32 \pm 0.12)\Delta_0 F_{1(s-v)} + (12.3 \pm 0.5), \quad (27)$$
$$N = 4,\ \Delta S = 0.6\ \text{kJ mol}^{-1},\ R = 0.80.$$

Correlation for carbonyl-containing compounds:

$$\Delta\mu_1 = (0.21 \pm 0.07)\Delta_0 F_{1(s-v)} + (9.6 \pm 0.7), \quad (28)$$
$$N = 6,\ \Delta S = 1.1\ \text{kJ mol}^{-1},\ R = 0.84.$$

All the obtained correlations correspond to variant 1; therewith, alcohols fall between variants 1a and 1b, and the other substances correspond to variant 1b. If activated solvates are on the solution surface, we can expect a correlation between $\Delta\mu_1$ and $\Delta H_{v(1)}$. In fact, such correlations are observed for all solutions in hexadecane [Eqs. (29)–(31)].

Correlation for alkanes:

$$\Delta\mu_1 = (0.71 \pm 0.05)\Delta H_{v(1)} + (-6.6 \pm 1.4), \quad (29)$$
$$N = 4,\ \Delta S = 0.12\ \text{kJ mol}^{-1},\ R = 0.999.$$

Correlation for carbonyl-containing molecules[1]:

$$\Delta\mu_1 = (0.81 \pm 0.17)\Delta H_{v(1)} + (-15.0 \pm 5.4), \quad (30)$$
$$N = 6,\ \Delta S = 0.7\ \text{kJ mol}^{-1},\ R = 0.995.$$

Correlation for alcohols:

$$\Delta\mu_1 = (0.65 \pm 0.02)\Delta H_{v(1)} + (-19.9 \pm 0.8), \quad (31)$$
$$N = 5,\ \Delta S = 0.15\ \text{kJ mol}^{-1},\ R = 0.981.$$

Comparison of correlations (26)–(28) and (29)–(31) shows a noticeable improvement of their quality.

Analysis of the properties of extremely dilute solutions in hexadecane shows that this solvent is able to separate solutes.

For analysis and description of the partial enthalpy of solvation of organic substances ($\Delta H_{1\text{soln,ex}}$), defined by Rudakov [8] as a difference between the enthalpies of interaction and cavity formation in an extremely dilute solution, weused the method of model thermodynamic functions of extremely dilute solutions. According to the conclusions in [3], the Helmholtz energy and internal energy of transfer of one particle from vapor into solution are close to each other. Their maximal difference does not exceed 3%. Therefore, experimental $\Delta H_{1\text{soln,ex}}$ and those calculated by the proposed method ($\Delta H_{1\text{soln,cal}}$) should fairly correlate with each other. We calculated $\Delta H_{1\text{soln,cal}}$ by Eq. (32) given in [2].

$$\Delta H_{1\text{soln,cal}} = \Delta U_{s,1} - 2RT + \Delta H_v. \quad (32)$$

As objects for comparison we have chose solutions of organic compounds in cyclohexane [9]. The results obtained are shown in Fig. 7. It is seen that the solutions under comparison, too, form two groups described by correlations (33) and (34).

The correlation for nonassociated substances is as follows:

$$\Delta H_{1\text{soln,ex}} = (0.88 \pm 0.06)\Delta H_{1\text{soln,cal}} + (-0.8 \pm 2.4), \quad (33)$$
$$N = 30,\ \Delta S = 3.8\ \text{kJ mol}^{-1},\ R = 0.95.$$

The correlation for associated substances is as follows:

$$\Delta H_{1\text{soln,ex}} = (1.53 \pm 0.1)\Delta H_{1\text{soln,cal}} + (-42.7 \pm 5.1), \quad (34)$$
$$N = 11,\ \Delta S = 2.6\ \text{kJ mol}^{-1},\ R = 0.98.$$

Our analysis shows that, in view of the change of the sign of the constant term (connected with the transfer of particles into solution but not backwards), the correlation for nonassociated substances corresponds to an intermediate variant between zero and 1a. For associated substances, a special correlation is observed. This result requires additional consideration. The point is that the b value is essentially higher than one and the a value is much higher than the heat of

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[1] In the calculation of $\Delta_0 F_{1(s-v)}$ for methyl acetate and ethyl formate, refined $I_{is,1}$ values were used (1522 and 1717 instead of 1737 and 1712 [1]), which did not affect substantially the resulting dependences.

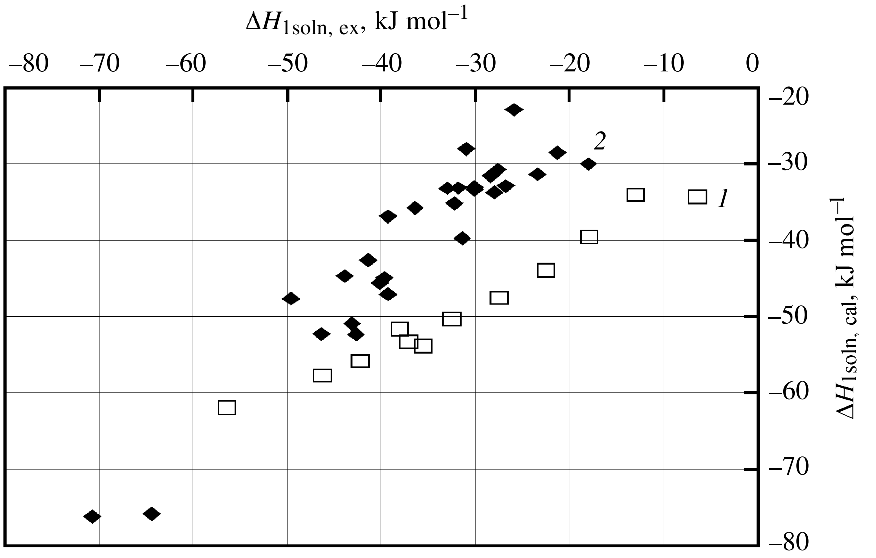

Fig. 7. Correlation of the calculated partial heats of solution in cyclohexane (I_{an} 0.01 kJ mol^{-1}, I_{is} 1248 kJ mol^{-1}, Λ_s 0.228, Φ_n 0.256) for a series of substances with experimental values. (*1*) Associated substances; (*2*) nonassociated substances. Methanol −13.0, −34.1; acetonitrile −18.0, −30.1; ethanol −18.0, −39.6; acetone −21.3, −28.6; 1-propan-1-ol −22.6, −43.9; butan-2-ol −26.8, −32.9; tetrahydrofuran −28.4, −31.6; methyl acetate −23.4, −31,4; butan-1-ol −27.6, −47.5; carbon disulfide −25.9, −23.0; benzene −30.1, −33.3; pyridine −31.4, −39.7; ethyl acetate −28, −33.8; pentan-1-ol −32.6, −50.3; 1-chlorobuthane −30.1, −33.2; aniline −38.1, −51.7; phenol −35.6, −53.8; fluorobenzene −31, −28.1; hexan-1-ol −37.2, −53.2; styrene −41.4, −42.6; heptan-2-ol −39.7, −45.0; heptan-1-ol −42.3, −55.8; chloroform −27.6, −30.8; acetophenone −42.7, −52.3; *N,N*-dimethylaniline −46.4, −47.7; nitrobenzene −43.1, −50.9; naphthalene −49.6, −47.6; octan-1-ol −46.4, −57.7; trichloroethylene −32.2, −35.2; benzaldehyde −39.3, −47.1; anisole 340.2, −45.7; chlorobenzene −36.4, −35.8; methyl benzoate −46.4, −52.3; iodomethane −24.2, −27.8; tetrachloromethane −31.8, −33.2; bromobenzene −39.3, −36.9; 1,1,2,2-tetrachloroethane −39.3, −43.4; benzophenone −64.4, −75.8; *trans*-azobenzene −70.7, −76.2; and iodobenzene −43.9; −44.7 (values of $\Delta H_{1\text{soln, cal}}$ are printed bold).

vaporization of cyclohexane. Furthermore, the correlation under consideration has a nonlinear character. These special features can result from the fact that cyclohexane contained a small admixture of components with higher anisotropic salvation potentials, for example water. Due to the selective solvation of alcohols with water, analogous correlation constants and nonlinear dependences can be obtained [2]. However, the choice in favor of this or that variant is possible only on the basis of additional investigations.

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REFERENCES

1. Gorodyskii, V.A., *Zh. Fiz. Khim.*, 2005, vol. 79, no. 6, p. 1040.
2. Gorodyskii, V.A., *Sol'vatokhromiya. Problemy i metody* (Solvatohromism. Problems and Methods), Bakhshiev, N.G., Ed., Leningrad: Leningr. Gos. Univ., 1989, p. 224.
3. Gorodyskii, V.A. and Moskvicheva, L.A., *Vestn. S.-Peterb. Gos. Univ., Ser. 4: Khim., Fiz.,* 1994, no. 1, p. 55.
4. Gorodyskii, V.A, *Vestn. S.-Peterb. Gos. Univ., Ser. 4: Khim., Fiz.,,* 1995, no. 4, p. 81.
5. Gorodyskii, V.A. and Arkhangel'skaya, A.B., *Zh. Obshch. Khim.,* 1995, vol. 65, no. 1, p. 7.
6. Gorodyskii, V.A., *Vestn. S.-Peterb. Gos. Univ., Ser. 4: Khim.,* Fiz., 1997, no. 1, p. 86
7. Solomonov, B.I. and Konovalov, A.I., *Usp. Khim.,* 1991, vol. 80, p. 45.
8. Rudakov, E.S., *Termodinamika mezhmolekulyarnogo vzaimodeistviya* (Thermodynamics of Intermolecular Interaction), Novosibirsk: Nauka, 1968.
9. Solomonov, B.I., Antipin, I.S., Novikov, V.B., and Konovalov, A.I., *Zh. Obshch. Khim.,* 1982, vol. 52, no. 12, p. 2681.
10. Gorodyskii, V.A. and Stepanova, N.A., *Opt. Spektrosk.,* 1986, vol. 60, no. 3, p. 511.
11. Gorodyskii, V.A. and Bakhshiev, N.G., *Opt. Spektrosk.,* 1971, vol. 31, no. 1, p. 218.