Russian Journal of General Chemistry, Vol. 72, No. 6, 2002, pp. 854–863. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 6, 2002, pp. 915–925.

Multiparameter Correlations for Description of Thermodynamic Parameters of Solvation: I. Enthalpy of Nonspecific Solvation

B. N. Solomonov, V. B. Novikov, and A. B. Solomonov

Kazan State University, Kazan, Tatarstan, Russia

Received July 13, 2000

Abstract—Applicability of a linear solvation-energy approach for descripition of the solvation enthalpies of nonelectrolytes is examined. In most cases a good fit of experimental solvation enthalpies can be attained. However, the resulting data are difficult to interpret in terms of different types of intermolecular interactions.

Quantitative relationships between structures and thermodynamic parameters of solvation of a wide range of organic nonelectrolytes were first obtained in [1, 2]. In particular, it was found that the solvation enthalpies of compounds of different classes (A_i) in cyclohexane (**I**) are linearly related to their molar refractions (MR_{A_i}).

$$-\Delta H_{\text{solv}}^{A_i/\mathbf{I}} = 4.39 + 1.05MR_{A_i}, \text{ kJ/mol.} \quad (1)$$

However, it was already clear from the cited works that this relationship is not universal. Thus the solvation enthalpies of linear and cyclic alkanes in cyclohexane were described by different dependences on MR_{A_i}. Moreover, there were different equations for normal and branched aliphatic derivatives. In this connection, corrections for branching were introduced (constant values) [2].

Equation (1) was improved [3] by adding the molar volume of solute ($V_M^{A_i}$), a parameter that accounts for void formation[1] in solvent S [Eq. (2)].

$$-\Delta H_{\text{solv}}^{A_i/\text{S}} = aMR_{A_i} + bV_M^{A_i}, \text{ kJ/mol.} \quad (2)$$

Here a and b are variables characterizing the given solvent.

The correlation quality was thus improved. Therewith, no attention was paid to the fact that MR_{A_i} correlates with $V_M^{A_i}$, which is inadmissible in constructing multiparameter correlations. Equation (2) was in essence the first multiparameter equation relating thermodynamic parameters of solvation to solute parameters.

Later [4] equation (2) was adapted to fit log L_{16}, a value proportional to the free energy of solvation in cyclohexane. An additional term was introduced, proportional to the squared dipole moment of solute, to account for polar solute–solvent (hexadecane) interactions [Eq. (3)]:

$$\log L_{16} = d + aMR_{A_i} + bV_M^{A_i} + c(\mu_{A_i})^2. \quad (3)$$

Here a, b, c, and d are variables and μ_{A_i} is the dipole moment of solute. Equation (3) fairly fitted logL_{16} for 84 compounds. The standard deviation (S_0) and correlation coefficient (R), obtained in [4], were 0.18 and 0.986, respectively. Therewith, MR_{A_i} was found to correlate with $V_M^{A_i}$ (R 0.972).

To go around the correlation between MR_{A_i} and $V_M^{A_i}$, the parameter MR_{A_i} in Eq. (3) was replaced by the parameters $f(n)$, $Q(n)$, and n, that relate to dispersion interaction [5].

$$f(n) = (n^2 - 1)/(n^2 + 2), \; Q(n) = (n^2 - 1)/(2n^2 + 2).$$

Here n is the refractive index. These three parameters do not correlate with $V_M^{A_i}$.

The results proved to be unexpected. The replacement of MR_{A_i} by $f(n)$, $Q(n)$, and n in Eq. (3) resulted in a better correlation (the standard deviation decreased almost three times). However, the fact that the coefficients at $V_M^{A_i}$ are positive values suggests that the void formation in hexadecane is an exothermic process, which, as also admmited by Dallas and Carr [5], is “physically absurdly.” Thus, the referees, voluntarily or not, were the first to call attention to the general problem of the feasibility of multiparameter

---

[1] Actually, it was suggested in [1, 2] that the molar refraction of solute is a measure both of solute–solvent dispersion interaction and of the solute volume.

correlation equations for description of thermodynamic parameters of solvation. This problem, in our opinion, is that the attainment of a better quantitative description not necessarily provides a deeper insight into the nature of intermolecular interactions underlying the thermodynamics of solvation.

Over the last decade most solvation studies made use of the linear solvation-energy relationships (LSER) formulated by Taft and Kamlet [6]. Abraham [4, 7] and Carr [8] extended this approach on thermodynamic parameters of solvation and transfer. According to this approach, the thermodynamic parameter (TP) of solvation or transfer depends on a number of solute parameters [Eqs. (4) and (5)]:

$$\mathrm{TP} = i + vV_x + s\pi_2^H + rR_2 + a\Sigma\alpha_2^H + b\Sigma\beta_2^H, \quad (4)$$

$$\mathrm{TP} = i + l\log L_{16} + s\pi_2^H + d\delta_2 + a\Sigma\alpha_2^H + b\Sigma\beta_2^H. \quad (5)$$

Here V_x is the McGowan characteristic volume [9], which, along with $\log L_{16}$, defines the contributions into TP of void formation and general dispersion interaction [7], π_2^H relates to the ability of solute to dipole and induction interactions with solvent, R_2 is the excess molar refraction [10], δ_2 is an empirical correction factor which compensates for the impossibility of describing electrostatic interactions by a single parameter (0 for aliphatic compounds, 0.5 for polychlorinated aromatic compounds, and 1 for any other aromatic compound) [8], $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ are the apparent acidity and basicity of solute [11]. The first three terms of Eqs. (4) and (5) relate to nonspecific solvation and the latter two, specific solute–solvent interaction.

The coefficients *i*, *v*, *l*, *s*, *r*, *d*, *a*, and *b* characterize the given solvent and are found by the multiple linear regression technique.

In the present work we analyzed feasibility of equations like (4) and (5) for descripition of the solvation enthalpies of nonelectolytes (36 solvents, 1538 solvation enthalpies). Analysis was performed both in terms of quantitative descripition and in terms of interpretation of the resulting coefficients (*i*, *v*, *l*, *s*, *r*, *d*, *a*, and *b*) and physical sence of their underlying contributions into the enthalpy of solvation. Along with Eqs. (4) and (5), we employed our own equation:

$$\Delta H_{\mathrm{solv}}^{A_i/\mathrm{S}} = i + h\Delta H_{\mathrm{solv}}^{A_i/\mathrm{I}} + s\pi_2^H + rR_2 + a\Sigma\alpha_2^H + b\Sigma\beta_2^H. \quad (6)$$

Here *h* is a variable depending on solvent. This equation differs from Eq. (5) in that it includes, instead of $\log L_{16}$, the enthalpy of solvation in cyclohexane ($\Delta H_{\mathrm{solv}}^{A_i/\mathrm{I}}$) as the parameter defining the energies of void formation and general dispersion interaction. The replacement of a value proportional to the free energy of solvation in cyclohexane by the enthalpy of solvation in cyclohexane should not affect interpretion of the resulting parameters, since the free energies and the enthalpies of solvation of alkanes are linearly related to each other [12]. Moreover, we introduced in Eq. (6) the parameter R_2 which, in our opinion, is better substantiated in terms of physical sence than δ_2.

In calculations by Eqs. (4)–(6) we largely relied on published enthalpies of solvation. Therewith, the number of solutes was 183, and they included nonelectrolytes of different classes, specifically inert gases, alkanes, alkenes, aromatic hydrocarbons, halogenated hydrocarbons, alcohols, phenols, ethers and esters, ketones, amines, amides, nitro compounds, etc. In cases where the enthalpies of solution ($\Delta H_{\mathrm{sol}}^{A_i/\mathrm{S}}$) were only available, the enthalpies of solvation were calculated by Eq. (7):

$$\Delta H_{\mathrm{solv}}^{A_i/\mathrm{S}} = \Delta H_{\mathrm{sol}}^{A_i/\mathrm{S}} - \Delta H_{\mathrm{vap}}^{A_i}. \quad (7)$$

Here $\Delta H_{\mathrm{vap}}^{A_i}$ is the enthalpy of vaporization of compound A_i at 298 K. The enthalpies of solution and solvation were taken from [1,2, 13–64], and the enthalpies of vaporization, from [8, 15, 20, 24, 30, 31, 42–45, 58, 65–70]. In cases where several values were available, more recent ones were preferred. The parameters of solutes ($\log L_{16}$, π_2^H, $\Sigma\alpha_2^H$, and $\Sigma\beta_2^H$) were taken from [7, 11, 71]. Some V_x, R_2, and δ_2 parameters were taken from [8, 71, 72] and some were calculated by the procedures described in [8, 9, 10]. In calculations by Eqs. (4), (5), and (6) were included only those solvents for which no less than 15 experimental points were available.

The calculation procedure is described in Experimental. For certain solvents the coefficients *a* and *b* were not calculated and let be zero. In this case, in the corresponding sites of Table 1 we omitted *a* and *b* values, implying without calculations that the given solvent cannot act as proton-acceptor or proton-donor. This conclusion was based on the zero values of the solvent parameters $\Sigma\beta_2^H$ and $\Sigma\alpha_2^H$, respectively. As judged from [7, 8], the authors of Eqs. (4) and (5) made use of just this approach, even though its validity is quite questionable. Under these circumstances, our aim was to obtain results at least comparable with the results in [7, 8].

The mean standard deviations for Eqs. (4)–(6) are equal to 2.41, 2.22, and 1.92 kJ/mol, and we can state with assurance that Eqs. (4)–(6) fairly describe the enthalpies of solvation of nonelectrolytes. The results of calculations by Eq. (6) are listed in Table 1. It proved that the worse correlation is obtained by

Eq. (4). One of the most probable reasons for this result is that isomeric compounds have equal V_x but different enthalpies of solvation. In the case of Eqs. (5) and (6), the $\log L_{16}$ and $\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}}$ values, as well as $\Delta H_{\mathrm{solv}}^{A_i/\mathrm{S}}$ for isomeric compounds are different. It should be noted that all the three equations provide acceptable results for all the solvents, except for 2,2,2-trifluoroethanol.

Authors that employ the LSER principle always stress that this principle not only possesses a predictive power, but also is an excellent tool for gaining insight into intermolecular interactions in solution.

Before passing to analysis of the physical sence of the results obtained in terms of the LSER principle, let us choose the basic equation. We prefer Eq. (6) by the following reasons. First, it provides slightly better correlation parameters, and, second, it includes in the left- and right-hand parts the enthalpy of solvation, which, as we will see further, mach facilitates interpretation. Therewith, it will be borne in mind that the choice of the basic equation is explained exclusively by brevity reasons, since respective coefficients of Eqs. (4)–(6) fairly correlate with each other, and, therefore, the essence of reasoning will be unchanged.

The term ($h\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}}$) contributes most into the enthalpy of nonspecific solvation (up to 95% for large molecules). By analogy with (vV_x) and ($l\log L_{16}$), this term should include the energy of general dispersion interaction and the enthalpy of void formation. The term "general dispersion interaction" was introduced in [7, 8] and apparently has to do with the dispersion interaction in a two-component system, where both components are alkanes. The authors of this approach suggest that vV_x or $l\log \mathrm{L}_{16}$ (in our case, $h\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}}$) are presently impossible to separate into the energy of solvent void formation and the energy of disperion interaction with solvent [7]. But what does the term $h\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}}$ mean? As follows from the results in Table 1, the free term of Eq. (6) is close to zero and thus is statistically insignificant. Taking into account that for alkanes (Y_i) $\pi_2^H = 0$, $R_2 = 0$, $\Sigma\alpha_2^H = 0$, and $\Sigma\beta_2^H = 0$, we obtain Eq. (8):

$$\Delta H_{\mathrm{solv}}^{Y_i/\mathrm{S}} \approx h\Delta H_{\mathrm{solv}}^{Y_i/\mathbf{I}}. \tag{8}$$

From here the coefficient h is given by (9):

$$h \approx \Delta H_{\mathrm{solv}}^{Y_i/\mathrm{S}}/\Delta H_{\mathrm{solv}}^{Y_i/\mathbf{I}}. \tag{9}$$

The figure compares the h values calculated by Eq. (9) and by the LSER method by Eq. (6) (Table 1). In calculations by Eq. (9) we took hexane as alkane Y_i because of the availability of its enthalpies of solution in most solvents. In whole, a fair fit is observed. It should, however, been noted that the largest deviations from the straight line (slope 45°) are characteristic of those solvents, where the basic set of solutes comprises few alkanes and alkyl-substituted compounds. To check Eq. (6) (Table 1) for universality, we excluded alkanes and alkyl-substituted compounds from the set of solutes.

Table 2 lists the results of calculations by Eq. (6) for the reduced database. For the solvents listed in the table, no less than 14 experimental point were available. The quality of the correlations in Table 2 is slightly higher than of those in Table 1, whereas the confidence ranges for h are much increased. However, the h values differ considerably from those obtained by Eq. (9) and by Eq. (6) for the initial database (Table 1). Simple calculation shows that the enthalpies of solvation of alkanes in these solvents will be predicted with a very large error. This fact suggests that the h value depends to a certain extent on solute database. However, even with a sufficiently large solute database, another difficulty associated with interpretation of these terms (vV_x, $l\log L_{16}$, and $h\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}}$) still remains. From Eq. (9) we obtain Eq. (10).

$$h\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}} \approx (\Delta H_{\mathrm{solv}}^{Y_i/\mathrm{S}}/\Delta H_{\mathrm{solv}}^{Y_i/\mathbf{I}})\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}}. \tag{10}$$

Earlier in [13, 46] we showed that the enthalpies of void formation in a series of solvents $\{\delta H_{\mathrm{void}}\}_{\mathrm{S}_0}^{\mathrm{S}}$ vary in parallel with the enthalpies of solution or solvation of alkanes in these solvents [Eq. (11)].

$$\{\delta H_{\mathrm{sol}}^{Y_i}\}_{\mathrm{S}_0}^{\mathrm{S}} = \Delta H_{\mathrm{sol}}^{Y_i/\mathrm{S}} - \Delta H_{\mathrm{sol}}^{Y_i/\mathrm{S}_0} = \Delta H_{\mathrm{sol}}^{Y_i/\mathrm{S}} - \Delta H_{\mathrm{solv}}^{Y_i/\mathrm{S}_0}. \tag{11}$$

Here S_0 is a solvent chosen as standard. In terms of this approach, comparison of $h\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}}$ for various solvents is equivalent to comparison of the enthalpies of void formation in these solvents [Eq. (12)].

$$h(\mathrm{S})\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}} - h(\mathrm{S}_0)\Delta H_{\mathrm{solv}}^{A/\mathbf{I}} = \frac{\{\delta H_{\mathrm{void}}^{Y_i}\}_{\mathrm{S}_0}^{\mathrm{S}}}{\Delta H_{\mathrm{solv}}^{Y_i/\mathbf{I}}}\,\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}}\,. \tag{12}$$

Here $h(\mathrm{S})$ and $h(\mathrm{S}_0)$ are the h values for solvents S and S_0. The enthalpy of solvation in cyclohexane can be represented as a sum of the enthalpy of void formation for A_i in cyclohexane ($\Delta H_{\mathrm{void}}^{A_i/\mathbf{I}}$) and the enthalpy of interaction of A_i with cyclohexane ($\Delta H_{\mathrm{int}}^{A_i/\mathbf{I}}$) [Eq. (13)]:

$$\Delta H_{\mathrm{solv}}^{A_i/\mathbf{I}} = \Delta H_{\mathrm{void}}^{A_i/\mathbf{I}} + \Delta H_{\mathrm{int}}^{A_i/\mathbf{I}}. \tag{13}$$

The latter term relates to general dispersion interaction. Accounting for Eq. (9) gives Eq. (14).

Table 1. Parameters of Eq. (6) for calculation of the enthalpies of solvation (kJ/mol) of various solutes in various solvents (*N* is the number of points)

No.	Solvent	*N*	*R*	S_0	*i*	*h*	*s*	*r*	*a*	*b*
1	Hexane	31	0.998	0.85	0.71 ± 0.70	1.05 ± 0.01	0.71 ± 0.71	–0.15 ± 0.63	–	–
2	Heptane	38	0.998	0.82	0.75 ± 0.46	1.06 ± 0.01	0.95 ± 0.61	–0.69 ± 0.66	–	–
3	Hexadecane	76	0.974	3.30	–0.42 ± 0.92	1.00 ± 0.03	–1.33 ± 1.76	0.79 ± 2.03	–	–
4	Benzene	77	0.991	1.54	0.64 ± 0.73	0.92 ± 0.02	–14.05 ± 0.63	2.46 ± 0.63	–11.02 ± 1.18	–
5	Toluene	66	0.996	1.02	0.02 ± 0.55	0.96 ± 0.01	–12.72 ± 0.55	3.37 ± 0.49	–12.50 ± 0.89	–
6	*p*-Xylene	17	0.999	0.64	1.80 ± 0.68	1.04 ± 0.01	–15.86 ± 1.52	7.09 ± 1.01	–9.05 ± 1.24	–
7	Mesitylene	36	0.996	1.17	0.84 ± 0.73	1.03 ± 0.02	–10.25 ± 0.90	4.08 ± 1.08	–14.35 ± 1.27	–
8	1,2-Dichloroethane	54	0.986	1.86	–0.26 ± 1.19	0.81 ± 0.03	–13.79 ± 1.42	0.11 ± 1.08	–12.31 ± 1.87	–7.82 ± 1.75
9	Chloroform	43	0.992	1.56	–0.59 ± 1.04	0.93 ± 0.03	–11.31 ± 1.19	2.90 ± 1.04	–4.91 ± 1.84	–18.66 ± 1.42
10	Tetrachloromethane	76	0.992	1.41	–1.90 ± 0.65	0.96 ± 0.02	–8.54 ± 0.63	2.33 ± 0.59	–	–
11	Chlorobenzene	17	0.998	0.94	1.09 ± 1.13	0.99 ± 0.02	–17.10 ± 2.31	6.95 ± 1.51	–9.03 ± 2.56	–
12	Trifluoromethylbenzene	33	0.994	1.30	–0.88 ± 0.85	0.92 ± 0.02	–16.72 ± 1.03	7.18 ± 1.21	–7.25 ± 1.59	–
13	Perfluoro-1,3-dimethylcyclohexane	38	0.959	2.26	5.44 ± 1.65	0.83 ± 0.05	–2.60 ± 1.59	–3.56 ± 2.20	–25.48 ± 4.61	–
14	Methanol	88	0.972	2.62	–2.38 ± 1.18	0.80 ± 0.03	0.08 ± 1.41	–6.35 ± 1.25	–38.50 ± 2.03	–20.71 ± 1.60
15	1-Hexanol	29	0.969	3.05	–0.75 ± 3.54	1.01 ± 0.10	2.73 ± 3.98	–3.40 ± 3.17	–44.60 ± 3.79	–3.88 ± 4.22
16	1-Octanol	32	0.987	2.45	0.96 ± 1.95	1.03 ± 0.04	9.63 ± 2.94	–6.85 ± 2.85	–54.58 ± 3.19	–12.19 ± 3.03
17	2,2,2-Trifluoroehanol	29	0.924	7.57	2.66 ± 7.21	0.75 ± 0.19	20.58 ± 8.02	–12.46 ± 7.42	–16.23 ± 8.91	–80.52 ± 8.28
18	2-Methyl-2-propanol	42	0.963	3.30	1.16 ± 2.38	0.93 ± 0.05	4.83 ± 3.09	–0.59 ± 2.43	–50.05 ± 3.35	–17.11 ± 3.23
19	Dipropyl ether	16	0.997	1.08	1.27 ± 1.35	0.99 ± 0.04	–10.13 ± 1.63	1.02 ± 1.14	–38.16 ± 1.62	–
20	Dibutyl ether	33	0.995	1.34	–0.16 ± 0.92	1.02 ± 0.02	–4.85 ± 1.06	0.53 ± 1.17	–38.62 ± 1.64	–
21	THF	21	0.994	1.87	2.15 ± 1.74	0.98 ± 0.04	–18.25 ± 2.77	3.22 ± 2.05	–33.57 ± 2.20	–
22	1,4-Dioxane	33	0.994	1.53	1.19 ± 1.20	0.84 ± 0.03	–19.04 ± 1.47	1.42 ± 1.04	–31.91 ± 1.50	–
23	Ethyl acetate	54	0.993	1.49	–1.42 ± 0.87	0.84 ± 0.02	–15.34 ± 0.87	1.27 ± 0.71	–35.47 ± 1.32	–
24	Acetone	37	0.990	1.76	–0.20 ± 1.27	0.82 ± 0.03	–14.86 ± 2.07	0.37 ± 1.35	–34.46 ± 1.82	–4.33 ± 2.27
25	Acetophenone	15	0.998	1.05	2.16 ± 1.04	0.93 ± 0.02	–18.42 ± 1.22	4.15 ± 1.85	–38.06 ± 1.72	–
26	Triethylamine	37	0.973	3.41	1.12 ± 2.25	1.07 ± 0.05	–2.66 ± 2.64	–2.96 ± 3.00	–58.71 ± 3.08	–
27	Aniline	19	0.987	1.62	–3.02 ± 2.68	0.52 ± 0.11	–14.56 ± 2.71	–5.18 ± 4.05	–22.61 ± 4.12	–18.13 ± 2.93
28	Nitrobenzene	21	0.994	1.50	2.16 ± 1.33	0.94 ± 0.03	–16.19 ± 1.23	2.29 ± 1.67	–20.42 ± 1.70	–
29	Acetonitrile	35	0.994	1.29	0.62 ± 1.15	0.74 ± 0.04	–17.67 ± 1.60	1.56 ± 1.28	–26.78 ± 1.44	–7.83 ± 1.80
30	Benzonitrile	24	0.997	0.93	0.14 ± 0.89	0.92 ± 0.02	–17.45 ± 1.18	5.41 ± 0.69	–30.14 ± 1.31	–
31	Formamide	23	0.991	1.86	1.70 ± 1.69	0.87 ± 0.04	–6.92 ± 2.52	0.61 ± 2.69	–32.29 ± 1.97	–21.02 ± 3.66
32	DMF	77	0.990	1.98	0.70 ± 0.90	0.80 ± 0.02	–19.50 ± 0.90	0.06 ± 0.82	–48.03 ± 1.46	–
33	Pyridine	34	0.983	2.29	1.10 ± 2.17	0.94 ± 0.07	–15.12 ± 1.99	2.92 ± 1.66	–47.74 ± 2.37	–
34	DMSO	56	0.982	2.56	–0.91 ± 1.66	0.66 ± 0.04	–17.66 ± 1.30	–2.95 ± 1.22	–51.57 ± 1.99	–
35	Acetic acid	21	0.974	2.38	3.95 ± 3.39	0.90 ± 0.08	–9.87 ± 4.06	–0.04 ± 4.54	–30.90 ± 3.33	–19.90 ± 6.98

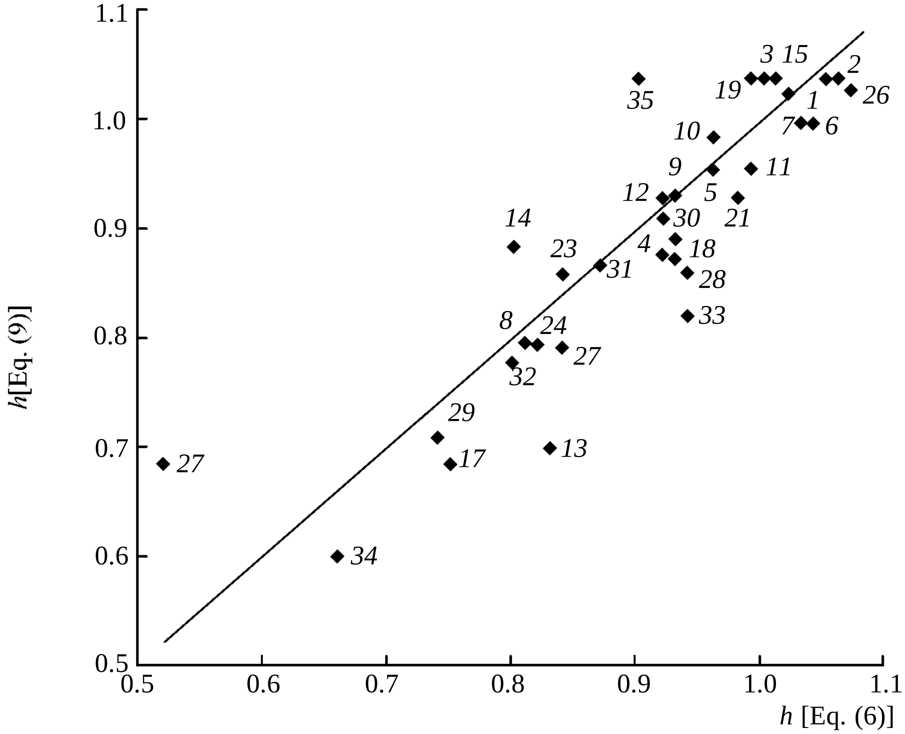
Table 2. Parameters of Eq. (6) for calculation of the enthalpies of solvation (kJ/mol) of solutes containing no alkyl groups (*N* is the number of points)

No.	Solvent	*N*	*R*	S_0	*i*	*h*	*s*	*r*	*a*	*b*
1	Hexadecane	14	0.883	5.28	–8.70 ± 5.23	0.74 ± 0.39	–20.48 ± 7.63	19.58 ± 16.44	–	–
2	Benzene	18	0.996	1.23	0.33 ± 2.37	0.90 ± 0.12	–16.53 ± 2.48	3.73 ± 2.76	–7.59 ± 1.88	–
3	Toluene	20	0.998	0.78	1.38 ± 1.37	1.02 ± 0.06	–14.77 ± 1.17	6.14 ± 1.46	–11.01 ± 1.21	–
4	1,2-Dichloroethane	14	0.998	1.00	3.01 ± 2.16	1.02 ± 0.13	–14.01 ± 3.82	6.10 ± 2.51	–11.01 ± 1.97	–8.79 ± 3.04
5	Chloroform	18	0.997	1.25	2.06 ± 2.20	1.07 ± 0.12	–8.89 ± 3.39	4.58 ± 2.68	–6.70 ± 2.04	–19.99 ± 3.43
6	Tetrachloromethane	23	0.998	0.86	–0.82 ± 1.41	0.89 ± 0.07	–11.40 ± 1.24	0.83 ± 1.79	–	–
7	Methanol	17	0.990	1.53	3.12 ± 3.18	1.25 ± 0.19	–1.71 ± 3.93	7.34 ± 4.75	–34.59 ± 2.57	–16.62 ± 3.47
8	1-Hexanol	16	0.977	2.44	1.15 ± 5.51	1.06 ± 0.33	–0.30 ± 5.86	–0.44 ± 8.58	–35.20 ± 4.27	–7.04 ± 5.55
9	THF	16	0.991	1.95	2.89 ± 3.95	1.13 ± 0.20	–15.19 ± 4.41	6.27 ± 4.46	–34.30 ± 3.33	–
10	1,4-Dioxane	18	0.992	1.87	4.29 ± 3.60	1.03 ± 0.19	–18.47 ± 5.07	6.16 ± 4.45	–32.47 ± 3.23	–
11	Ethyl acetate	17	0.998	0.88	1.93 ± 1.78	1.02 ± 0.09	–18.88 ± 1.77	8.30 ± 2.02	–33.65 ± 1.49	–
12	Acetonitrile	19	0.996	1.31	5.20 ± 2.48	1.07 ± 0.14	–13.48 ± 3.78	8.74 ± 3.04	–27.09 ± 2.31	–13.42 ± 4.25
13	DMF	19	0.988	2.29	5.82 ± 4.15	1.13 ± 0.23	–19.00 ± 4.58	8.66 ± 5.31	–45.26 ± 3.51	–
14	Pyridine	19	0.990	2.07	5.18 ± 3.96	1.02 ± 0.19	–20.12 ± 3.74	6.44 ± 4.61	–44.49 ± 3.16	–
15	DMSO	19	0.988	2.28	3.81 ± 4.37	0.88 ± 0.21	–21.29 ± 4.14	4.66 ± 5.09	–46.88 ± 3.48	–

$$h\Delta H_{\text{solv}}^{A_i/\mathbf{I}} \approx \frac{\Delta H_{\text{solv}}^{Y_i/\text{S}}}{\Delta H_{\text{solv}}^{Y_i/\mathbf{I}}} \quad (\Delta H_{\text{void}}^{A_i/\mathbf{I}} + \Delta H_{\text{int}}^{A_i/\mathbf{I}}). \tag{14}$$

We consider Eq. (14) impossible to interpret as a sum of the enthalpy of void formation in solvent S and of the enthalpy of general dispersion interaction, unless some assumptions are made.

According to Abraham [7] and Carr [8], the rest of nonspecific solvation is estimated by the terms rR_2



Comparison of the *h* values for various solvents, calculated by Eqs. (6) and (9) (the solvent numbers are given in Table 1).

and $s\pi_2^H$. The general dispersion interaction does not exhaust the whole solute–solvent dispersion interaction. Therefore, Abraham [10] introduced an additional term rR_2, where r is a variable and R_2 is determined by Eq. (15).

$$R_2 = MR_{A_i} - MR_{Y_i} \text{ (provided } V_x^{A_i} = V_x^{Y_i}). \quad (15)$$

There is an excellent correlation between MR_{Y_i} and $V_x^{Y_i}$, which allows us to calculate MR_{Y_i} for any $V_x^{Y_i}$. Since MR_{A_i} correlates with the energy of dispersion interaction, the term rR_2 has the following physical sense. If we take two molecules with equal volumes, one of which is alkane, and exclude all interactions, except for dispersion, then the difference in the enthalpies or free energies of solvation of these two molecules will be equal to the product rR_2. The latter is additional dispersion interaction, while r, according to Abraham [10], reflects the ability of solvent to dispersion interactions with π and n electrons of solute, which is characteristic of all organic compounds, except for alkanes.

The interpretation of the constant π_2^H is difficult to understand. First, this interpretation varied with time. In earlier works [4, 72, 73] the constant π_2^H was considered to reflect solute dipolarity, but the term $s\pi_2^H$ was admitted “hardly interpreted,” since π_2^H includes, along with polarity, other contributions [14]. More recently, Abraham [7, 74] and Carr [8, 75] stated that π_2^H reflects polarity–polarizability of solute, while the product $s\pi_2^H$ was considered to account for dipole and dipole–induction solvent–solute interactions by Carr [8] and “plus some polarization interaction” by Abraham [7]. In his later works [7, 74] Abraham omitted these interactions. This indefiniteness in the interpretation of π_2^H is not accidental.

Solute and solvent molecules possess some polarizabilities α_{A_i} and α_S and some nonzero dipole moments μ_{A_i} and μ_S. It is quite unclear why the product $s\pi_2^H$ for alkanes is equal to zero, regardless of the fact the energy of dipole–induction interactions between a polar solvent and an alkane is nonzero. The practically zero free term in Eq. (6) gives us no way to explaining the zero π_2^H values for alkanes, as it was done in [8]. If we accept that π_2^H relates to solute dipolarity [4, 72, 73], then it is quite unclear why the π_2^H values for aromatic hydrocarbons with $\mu_{A_i} = 0$ are nonzero. It we accept, following Abraham [7, 74], that π_2^H relates to dipolarity and polarizability simultaneously, then another contradiction arises. In the case of solvation of nonpolar compounds by nonpolar solvents, such as carbon tetrachloride or benzene, a nature and should be accounted for in the terms nonzero term $s\pi_2^H$ appears, which is dispersion in $h\Delta H_{\text{solv}}^{A_i/\mathbf{I}}$ and rR_2.

Our calculations show that the sign of v has a physical sence only in the case of Eq. (4). With Eq. (6) (Table 1) the additional dispersion interaction term rR_2 is most frequently endothermic. The resulting $s\pi_2^H$ terms are hardly interpreted by the above reasons. However, with alcohols as solvents, this term is also endothermic, which makes no sense. The latter fact is inexplicable in terms of the peculiar features of alcohols as solvents associated by H bonding, since in acetic acid and formamide the term $s\pi_2^H$ is exothermic. It seems that the parameters of nonspecific solvation in Eqs. (4), (5), and (6) allow quantitative description of the enthalpies of solvation, but the resulting data are difficult to interpret in terms of physical sense. One more evidence for this impression comes from the calculated enthalpies of vaporization of liquid solutes (140 of the total of 183 solutes under consideration). The enthalpy of vaporization of A_i ($\Delta H_{\text{vap}}^{A_i}$) is equal but opposite in sign to the enthalpy of self-solvation of A_i ($\Delta H_{\text{solv}}^{A_i/A_i}$) [Eq. (16)]:

$$\Delta H_{\text{vap}}^{A_i} = -\Delta H_{\text{solv}}^{A_i/A_i}. \quad (16)$$

Two schemes were employed to calculate $\Delta H_{\text{solv}}^{A_i/A_i}$: traditional [Eqs. (5) and (6)] and by Eqs. (17a) and (17b).

$$\Delta H_{\text{solv}}^{A_i/A_i} = i + l\log L_{16} + s\pi_2^H + d\delta_2 + c\Sigma\alpha_2^H\Sigma\beta_2^H, \quad (17a)$$

$$\Delta H_{\text{solv}}^{A_i/A_i} = i + h\Delta H_{\text{solv}}^{A_i/\mathbf{I}} + s\pi_2^H + rR_2 + c\Sigma\alpha_2^H\Sigma\beta_2^H. \quad (17b)$$

Here $c\Sigma\alpha_2^H\Sigma\beta_2^H$ relates to specific interactions of solvent molecules with each other and, in our opinion, fully agrees with the ideology underlying Eqs. (4), (5), and (6). As seen from Table 3, equation (5), (6) and (17a), (17b) fit the enthalpies of vaporization no worse than the enthalpies of solvation in a single solvent, but the latter two equations should be preferred. However, the coefficients l, h, s, d, and r in such calculations make no physical sense.

Such an intricate phenomenon as solvation can apparently by described by a combination of several parameters. However, it is desirable, first, to do with as little parameters as possible and, second, that applicability of multiparameter correlations be not be estimated in terms of a quantitative criterion only.

Earlier we proposed [76] an alternative approach to calculation of the enthalpies of solvation [Eq. (18)].

$$\Delta H_{\text{solv}}^{A_i/S}(\text{nonsp}) = (\delta h^S - \delta h^{\mathbf{I}})V_x^{A_i} + \Delta H_{\text{solv}}^{A_i/\mathbf{I}} + q[(\Delta H_{\text{solv}}^{A_i/\mathbf{II}} - \Delta H_{\text{solv}}^{A_i/\mathbf{I}}) - (\delta h^{\mathbf{II}} - \delta h^{\mathbf{I}})V_x^{A_i}] + w\omega. \quad (18)$$

This approach is based on comparison of the en-

Table 3. Parameters for calculation of the enthalpies of vaporization (kJ/mol) by Eqs. (5), (6), (17a), and (17b) (N is the number of points)

Equation no.	N	R	S_0	i	l	h	s
5	140	0.978	2.25	–5.59 ± 0.75	–9.32 ± 0.21	–	–5.56 ± 1.02
6	136	0.970	2.64	0.63 ± 1.01	–	1.02 ± 0.03	–7.48 ± 1.27
17a	140	0.979	2.17	–6.78 ± 0.71	–9.01 ± 0.19	–	–9.46 ± 0.74
17b	136	0.984	1.94	–0.18 ± 0.73	–	1.01 ± 0.02	–12.40 ± 0.66

Equation no.	d	r	a	b	c
5	3.66 ± 0.59	–	–40.62 ± 1.39	–6.30 ± 1.20	–
6	–	2.97 ± 1.08	–41.57 ± 1.72	–7.04 ± 1.48	–
17a	4.36 ± 0.51	–	–	–	–95.51 ± 2.85
17b	–	5.53 ± 0.68	–	–	–102.87 ± 2.66

Table 4. Specific enthalpies of void formation (δh^S) for certain solvents [kJ × 100/(mol cm^3)] and parameters of Eq. (18) for calculation of the enthalpies of nonspecific solvation (kJ/mol) in various solvents (N is the numer of points)

No.	Solvent	δh^S	N	R	S_0	q	w
1	Benzene	5.02	52	0.991	1.09	1.55 ± 0.03	–0.76 ± 0.20
2	Toluene	2.65	46	0.991	0.82	1.32 ± 0.03	–0.60 ± 0.15
3	*p*-Xylene	1.31	14	0.983	0.89	0.89 ± 0.09	–1.13 ± 0.40
4	Mesitylene	1.10	30	0.964	1.11	0.99 ± 0.06	–0.70 ± 0.36
5	1,2-Dichloroethane	8.56	42	0.991	1.53	2.31 ± 0.05	–0.57 ± 0.30
6	Chlorobenzene	2.56	15	0.997	0.50	1.08 ± 0.04	–1.12 ± 0.23
7	Trifluorobenzene	3.50	28	0.990	0.96	1.51 ± 0.05	0.05 ± 0.32
8	Dibutyl ether	0.53	27	0.971	0.66	0.67 ± 0.04	–1.04 ± 0.22
9	THF	3.37	17	0.996	0.96	1.45 ± 0.08	–4.09 ± 0.42
10	1,4-Dioxane	7.58	23	0.994	1.23	1.97 ± 0.05	–2.68 ± 0.30
11	Ethyl acetate	5.98	44	0.990	1.26	1.79 ± 0.04	–1.82 ± 0.24
12	Acetone	7.56	25	0.994	1.21	1.94 ± 0.04	–1.66 ± 0.27
13	Acetophenone	5.35	9	0.997	0.74	1.86 ± 0.09	–1.18 ± 0.72
14	Triethylamine	0.43	28	0.941	0.87	0.63 ± 0.05	–1.08 ± 0.30
15	Nitrobenzene	5.04	12	0.993	1.29	1.68 ± 0.08	–1.07 ± 0.55
16	Acetonitrile	10.22	23	0.997	0.98	2.20 ± 0.04	–0.44 ± 0.22
17	Benzonitrile	5.30	16	0.998	0.58	1.82 ± 0.03	–0.33 ± 0.16
18	DMF	8.78	46	0.992	1.42	2.29 ± 0.04	–2.64 ± 0.26
19	Pyridine	6.22	20	0.994	1.28	1.89 ± 0.05	–0.97 ± 0.30
20	DMSO	13.87	42	0.984	2.44	2.60 ± 0.08	–2.56 ± 0.45

thalpies of solvation in a given solvent S, cyclohexane (**I**), and carbon tetrachloride (**II**). The variable q shows how many times the relative enthalpy interaction of solutes with solvent S is higher that those with carbon tetrachloride. The solute parameter is more formal in nature. It was taken to be 1 for aromatic compounds, –1 for derivatives of aliphatic hydrocarbonds, and 0 for solutes containing both alkyl and aromatic substituents. The results of calculations by Eq. (18) are listed in Table 4. The mean standard deviation for 20 solvents is 1.09 kJ/mol. Thus, Eq. (18) compares with typical LSER equations [Eqs. (4)–(6)] in the quality of description of the enthalpies of solvation but includes much less variables.

Summarizing the aforesaid, we can draw the following conclusion. The LSER principle provides fair fit of experimental enthalpies of solvation. However, this principle is formal in nature and, therefore, the

Table 5. Mutual correlation parameters of solutes

Parameter	V_x	$\log L_{16}$	$\Delta H^{A_i/\mathbf{I}}_{\text{solv}}$	π_2^H	R_2	δ_2	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$
V_x	1.000	0.863	–0.907	0.119	0.198	0.165	–0.128	0.079
$\log L_{16}$	0.863	1.000	–0.986	0.577	0.641	0.526	0.043	0.222
$\Delta H^{A_i/\mathbf{I}}_{\text{solv}}$	–0.907	–0.986	1.000	–0.423	–0.507	–0.407	0.137	–0.170
π_2^H	0.119	0.577	–0.423	1.000	0.701	0.587	0.248	0.549
R_2	0.198	0.641	–0.507	0.701	1.000	0.821	0.173	0.066
δ_2	0.165	0.526	–0.407	0.587	0.821	1.000	0.093	0.014
$\Sigma\alpha_2^H$	–0.128	0.043	0.137	0.248	0.173	0.093	1.000	0.231
$\Sigma\beta_2^H$	0.079	0.222	–0.170	0.549	0.066	0.014	0.231	1.000

resulting data are difficult to interpret unambiguously in terms of contributions of different types of intermolecular interactions into the enthalpy of nonspecific solvation. We could demonstrate the possibility of quantitative description of the enthalpy of nonspecific solvation on the basis of much less formal assumptions.

Analyzing the results of calculations by Eqs. (4)–(6), we can note that the equations all give similar estimates for the contribution of specific interactions into the enthalpy of solvation ($a\Sigma\alpha_2^H + b\Sigma\beta_2^H$). Equation (18) we proposed here takes account of the enthalpy of nonspecific solvation only. A more detailed analysis of the contribution of specific interactions into the enthalpy of solvation, in terms of the LSER principle inclusive, will be the subject of our following communications.

EXPERIMENTAL

The experimental enthalpies of solvation, used in calculations, were obtained by Eq. (7). The enthalpies of vaporization were taken from the literature [8, 15, 20, 24, 30, 31, 42–45, 58, 65–70]. When several different published values were available, those obtained by calorimetry or found in more recent publications were usually preferred. The enthalpies of solution of nonelectrolytes in various solvents were mostly taken from our previous works [1, 2, 13, 22, 39, 46–50] and from works of other authors [15–21, 23–38, 40–45, 51–64]. Certain enthalpies of solution in cyclohexane and carbon tetrachloride we determined calorimetrically in the present work.

Solvents and solutes for calorimetric measurements were purified and dried by the procedure described in [77]. The residual water contents were determined by electrochemical titration in a waste Fischer reactive [78]. The resulting values for cyclohexane and carbon tetrachloride were less than 0.01 M.

The enthalpies of solution were determined at 298 K in a calorimeter similar to that described in [48]. The cell volume was 100 ml, the final solute concentration was no higher than 0.03 M. The enthalpy of solution was averaged over 4–6 runs. The resulting enthalpies of solution at 298 K in kJ/mol were 18.50 ± 0.14 (1-propanol in carbon tetrachloride), 2.02 ± 0.12 (diethyl ether in cyclohexane), and 10.73 ± 0.22 (acetophenone in cyclohexane).

Statistical calculations by Eqs. (4–6), (17), and (18) were performed by the multiple linear regression technique using the STATISTICA program.

In calculations by LSER equations, mutual linear correlation of solute parameters is inadmissible. The mutual correlation parameters of the solutes in study are given in Table 5. As seen from this table, the mutual correlation coefficients for parameters entering any of the LSER equation simultaneously are no higher than 0.701 (mutual correlation coefficient of π_2^H and R_2).

The linear regression analysis by Eqs. (4–6) and (17) involved optimization of the free term of the linear equation. Equation (18) was preliminarily linearized to obtain Eq. (19).

$$Y^{A_i/\mathrm{S}} = gY^{A_i/\mathbf{II}} + w\omega. \tag{19}$$

Here $Y^{A_i/\mathrm{S}} = \Delta H^{A_i/\mathrm{S}}_{\text{solv}} - \Delta H^{A_i/\mathbf{I}}_{\text{solv}} - (\delta h^{\mathrm{S}} - \delta h^{\mathbf{I}})V_x^{A_i}$. According to Eq. (13), the $Y^{A_i/\mathrm{S}}$ value is a difference between the enthalpies of interaction of solute with solvent S and cycloxehane, i.e. in calculations we used, instead of Eq. (18), its equivalent Eq. (19). Therewith, the free term i in the latter equation was taken to be a fixed value (zero). For this reason, the correlation coefficients obtained by these equations should not be compared with the corresponding characteristics for Eqs. (4)–(6) and (17).

Along with the correlation coefficients R, in the tables including the results of multiple regression analysis we also give S_0 values (standard deviations of points from the regression line). The values of variables, obtained by statistical calculations by Eqs. (6), (17), and (18), are given in the corresponding tables with their standard deviations.

REFERENCES

1. Solomonov, B.N., Antipin, I.S., Gorbachuk, V.V., and Konovalov, A.I., *Dokl. Akad. Nauk SSSR*, 1979, vol. 247, no. 2, p. 405.
2. Solomonov, B.N., Antipin, I.S., Novikov, V.B., and Konovalov, A.I., *Zh. Obshch. Khim.*, 1982, vol. 52, no. 12, p. 2681.
3. Fuchs, R., Chambers, E.J., and Stephenson, W.K., *Can. J. Chem.*, 1987, vol. 65, no. 11, p. 2624.
4. Abraham, M.H. and Fuchs, R., *J. Chem. Soc., Perkin Trans. 2*, 1988, no. 2, p. 523.
5. Dallas, A.J. and Carr, P.W., *J. Phys. Chem.*, 1994, vol. 98, no. 18, p. 4927.
6. Kamlet, M.J. and Taft, R.W., *J. Am. Chem. Soc.*, 1976, vol. 98, no. 2, p. 377.
7. Abraham, M.H., *Chem. Soc. Rev.*, 1993, vol. 2, no. 2, p. 73.
8. Sherman, S.R., Suleiman, D., Hait, M.J., Schiller, M., Liotta, C.L., Eckert, C.A., Li, J.J., Carr, P.W., Poe, R.B., and Rutan, S.C., *J. Phys. Chem.*, 1995, vol. 99, no. 28, p. 11239.
9. Abraham, M.H. and McGowan, J.C., *Chromatographia*, 1987, vol. 23, no. 4, p. 243.
10. Abraham, M.H., Whiting, G.S., Doherty, R.M., and Shuely, W.J., *J. Chem. Soc., Perkin Trans. 2*, 1990, no. 8, p. 1451.
11. Abraham, M.H., *J. Phys. Org. Chem.*, 1993, vol. 6, no. 1, p. 660.
12. Solomonov, B.N., Gorbachuk, V.V., and Konovalov, A.I., *Zh. Obshch. Khim.*, 1982, vol. 52, no. 12, p. 2688.
13. Solomonov, B.N., Antipin, I.S., Gorbachuk, V.V., and Konovalov, A.I., *Dokl. Akad. Nauk SSSR*, 1978, vol. 243, no. 6, p. 1499.
14. Abraham, M.H., Whiting, G.S., Fuchs, R., and Chambers, E.J., *J. Chem. Soc., Perkin Trans. 2*, 1990, no. 2, p. 291.
15. Airoldi, C. and Roca, S., *J. Solution Chem.*, 1993, vol. 8, no. 8, p. 707.
16. Arnett, E.M. and Larsen, J.W., *J. Am. Chem. Soc.*, 1969, vol. 91, no. 6, p. 1438.
17. Arnett, E.M., Joris, L., Mitchell, E., Murty, T.S.S.R., Gorrie, T.M., and Schleyer, P.V.R., *J. Am. Chem. Soc.*, 1970, vol. 92, no. 8, p. 2365.
18. Arnett, E.M. and Carter, J.V., *J. Am. Chem. Soc.*, 1971, vol. 93, no. 6, p. 1516.
19. Arnett, E.M., Mitchell, E., and Murty, T.S.S.R., *J. Am. Chem. Soc.*, 1974, vol. 96, no. 12, p. 3875.
20. Arnett, E.M., Chawla, B., Bell, L., Taagepera, M., Hehre, W.J., and Taft, R.W., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 17, p. 5729.
21. Berling, D. and Olofsson, G., *J. Solution Chem.*, 1994, vol. 8, no. 8, p. 911.
22. Borisover, M.D., Stolov, A.A., Cherkasov, A.R., Izosimova, S.V., and Solomonov, B.N., *Zh. Fiz. Khim.*, 1994, vol. 68, no. 1, p. 56.
23. Catalan, J., Gomez, J., Couto, A., and Laynez, J., *J. Am. Chem. Soc.*, 1990, vol. 112, no. 5, p. 1678.
24. Dellagatta, G., Stradella, L., and Venturello, P., *J. Solution Chem.*, 1981, vol. 10, no. 3, p. 209.
25. Drago, R.S., Nozari, M.S., and Vogel, G.C., *J. Am. Chem. Soc.*, 1972, vol. 94, no. 1, p. 90.
26. Duer, W.C. and Bertrand, G.L., *J. Am. Chem. Soc.*, 1974, vol. 96, no. 5, p. 1300.
27. Fuchs, R., Cole, R.R., and Rodewald, R.F., *J. Am. Chem. Soc.*, 1972, vol. 94, no. 22, p. 8645.
28. Fuchs, R. and Rodewald, R.F., *J. Am. Chem. Soc.*, 1973, vol. 95, no. 18, p. 5897.
29. Fuchs, R., Young, T.M., and Rodewald, R.F., *J. Am. Chem. Soc.*, 1974, vol. 96, no. 14, p. 4705.
30. Fuchs, R., Peacock, L.A., and Das, K., *Can. J. Chem.*, 1980, vol. 58, no. 22, p. 2301.
31. Fuchs, R., Peacock, L.A., and Stephenson, W.K., *Can. J. Chem.*, 1982, vol. 60, no. 15, p. 1953.
32. Fuchs, R. and Stephenson, W.K., *Can. J. Chem.*, 1985, vol. 63, no. 1, p. 349.
33. Gerber, J.N. and Sawyer, D.N., *Anal. Chem.*, 1972, vol. 44, no. 7, p. 1199.
34. Goralski, P. and Tkaczyk, M., *J. Chem. Soc., Faraday Trans. 1*, 1987, vol. 83, no. 9, p. 3083.
35. Guitry, R.M. and Drago, R.S., *J. Phys. Chem.*, 1974, vol. 78, no. 4, p. 454.
36. Kiselev, V.D., Veisman, E.A., and Konovalov, A.I., Available from ONIITEKhim, 1980, Cherkassy, no. 253KhP-D80.
37. Krishnan, C.V. and Friedman, H.L., *J. Phys. Chem.*, 1971, vol. 75, no. 23, p. 3598.
38. Krishnan, C.V. and Friedman, H.L., *J. Phys. Chem.*, 1971, vol. 75, no. 3, p. 288.
39. Novikov, V.B., Stolov, A.A., Gorbatchuk, V.V., and Solomonov, B.N., *J. Phys. Org. Chem.*, 1998, vol. 11, no. 2, p. 283.
40. Ochkin, A.V., Vinetskaya, T.N., and Frolov, Yu.G., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1974, vol. 17, no. 5, p. 677.

41. Olofsson, G. and Olofsson, J., *J. Am. Chem. Soc.*, 1973, vol. 95, no. 22, p. 7231.
42. Parsons, G.H., Rochester, C.H., and Wood, C.E.C., *J. Chem. Soc. B*, 1971, no. 4, p. 533.
43. Rochester, C.H. and Waters, J.A., *J. Chem. Soc., Faraday Trans. 1*, 1982, vol. 78, no. 2, p. 631.
44. Saluja, P.S., Young, T.M., Rodewald, R.F., Fuchs, F.H., and Kohli, D., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 9, p. 2949.
45. Saluja, P.S., Peacock, L.A., and Fuchs, R., *J. Am. Chem. Soc.*, 1979, vol. 101, no. 6, p. 1958.
46. Solomonov, B.N., Antipin, I.S., Gorbachuk, V.V., and Konovalov, A.I., *Zh. Obshch. Khim.*, 1982, vol. 52, no. 10, p. 2154.
47. Solomonov, B.N., Novikov, V.B., Gorbachuk, V.V., and Konovalov, A.I., *Dokl. Akad. Nauk SSSR*, 1982, vol. 265, no. 6, p. 1441.
48. Solomonov, B.N., Konovalov, A.I., Novikov, V.B., Vedernikov, A.N., Borisover, M.D., and Gorbachuk, V.V., *Zh. Obshch. Khim.*, 1984, vol. 54, no. 7, p. 1622.
49. Solomonov, B.N., Konovalov, A.I., Novikov, V.B., Gorbachuk, V.V., and Neklyudov, S.A., *Zh. Obshch. Khim.*, 1985, vol. 55, no. 9, p. 1889.
50. Solomonov, B.N., Borisover, M.D., and Konovalov, A.I., *Zh. Obshch. Khim.*, 1987, vol. 57, no. 2, p. 423.
51. Spencer, J.N., Sweigart, J.R., Brown, M.E., Bensing, R.L., Hassinger, T.L., Kelly, W., Housel, D.L., Reisinger, G.W., Reifsnyder, D.S., Gleim, J.E., and Peiper, J.C., *J. Phys. Chem.*, 1977, vol. 81, no. 24, p. 2237.
52. Spencer, J.N., Gleim, J.E., Hackman, M.L., Blevins, C.H., and Garret, R.C., *J. Phys. Chem.*, 1978, vol. 82, no. 5, p. 563.
53. Spencer, J.N., Gleim, J.E., Blevins, C.H., Garret, R.C., and Mayer, F.J., *J. Phys. Chem.*, 1979, vol. 83, no. 20, p. 2615.
54. Spencer, J.N., Gleim, J.E., Blevins, C.H., Garret, R.C., and Mayer, F.J., *J. Phys. Chem.*, 1979, vol. 83, no. 10, p. 1249.
55. Spencer, J.N., Berger, E.M., Powell, C.R., Henning, B.D., Furman, G.S., Loffredo, W.M., Rydberg, E.M., Neubort, N.A., Shoop, C.E., and Slauch, D.N., *J. Phys. Chem.*, 1981, vol. 85, no. 9, p. 1236.
56. Spencer, J.N., Holmboe, E.S., Kirshenbaum, M.R., Barton, S.W., Smith, K.A., Wolbach, W.S., and Powell, J.F., *Can. J. Chem.*, 1982, vol. 60, no. 10, p. 1183.
57. Stephenson, W.K. and Fuchs, R., *Can. J. Chem.*, 1985, vol. 63, no. 2, p. 336.
58. Stephenson, W.K. and Fuchs, R., *Can. J. Chem.*, 1985, vol. 63, no. 9, p. 2540.
59. Stephenson, W.K. and Fuchs, R., *Can. J. Chem.*, 1985, vol. 63, no. 2, p. 342.
60. Stephenson, W.K. and Fuchs, R., *Can. J. Chem.*, 1985, vol. 63, no. 9, p. 2529.
61. Stephenson, W.K. and Fuchs, R., *Can. J. Chem.*, 1985, vol. 63, no. 9, p. 2535.
62. Stokes, R.H. and Burfitt, C., *J. Chem. Thermodyn.*, 1975, vol. 7, no. 8, p. 803.
63. Uruska, I. and Inerowicz, H., *J. Solution Chem.*, 1980, vol. 9, no. 2, p. 97.
64. Arnett, E.M. and McKelvey, D.R., *J. Am. Chem. Soc.*, 1966, vol. 88, no. 11, p. 2598.
65. Cox, J.D. and Pilcher, G., *Thermochemistry of Organic and Organometallic Compounds*, London: Academic, 1973.
66. Bystrom, K. and Mansson, M., *J. Chem. Soc., Perkin Trans. 2*, 1982, vol. 78, no. 5, p. 565.
67. Hossenlopp, J.A. and Scott, D.W., *J. Chem. Thermodyn.*, 1981, vol. 13, no. 5, p. 423.
68. Hossenlopp, J.A. and Scott, D.W., *J. Chem. Thermodyn.*, 1981, vol. 13, no. 5, p. 405.
69. Lebedev, Yu.A. and Miroshnichenko, E.A., *Termokhimiya paroobrazovaniya organicheskikh veshchestv* (Thermochemistry of Vaporization of Organic Compounds), Moscow: Nauka, 1981.
70. Rochester, C.H. and Symonds, J.R., *J. Chem. Soc., Faraday Trans. 1*, 1973, vol. 69, no. 7, p. 1267.
71. Abraham, M.H., Andonianhaftvan, J., Whiting, G.S., Leo, A., and Taft, R.S., *J. Chem. Soc., Perkin Trans. 2*, 1994, no. 8, p. 1777.
72. Abraham, M.H., Chadha, H.S., Whiting, G.S., and Mitchell, R.C., *J. Pharm. Sci.*, 1994, vol. 83, no. 8, p. 1085.
73. Abraham, M.H., Whiting, G.S., Doherty, R.M., and Shuely, W.J., *J. Chem. Soc., Perkin Trans. 2*, 1990, no. 9, p. 1851.
74. Abraham, M.H., Chadha, H.S., and Leo, A.J., *J. Chromatogr. A*, 1994, vol. 685, no. 2, p. 203.
75. Tan, L.C., Carr, P.W., and Abraham, M.H., *J. Chromatogr. A*, 1996, vol. 752, no. 1, p. 1.
76. Solomonov, B.N., Novikov, V.B., and Solomonov, A.B., *Zh. Fiz. Khim.*, 2000, vol. 74, no. 7, p. 1229.
77. *Organic Solvents: Physical Properties and Methods of Purification*, Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., Jr., Eds., New York: Interscience, 1955, 2nd ed.
78. Nichugovskii, G.F., *Opredelenie vlazhnosti khimicheskikh veshchestv* (Determination of Moisture Content of Organic Substances), Leningrad: Khimiya, 1977.