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Multiparameter Correlations for Describing Thermodynamic Parameters of Solvation: II.[1] Enthalpy of Specific Interaction

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Abstract—The applicability of the approach based on the linear solvation energy relationship to describing the enthalpies of specific solvent–solute interactions was examined. In associated solvents, this approach reflects the contribution of specific interaction incorrectly. Although the enthalpies of solvation as a whole are described well, this is an "occasional" result and is due to averaging over different compounds and redistribution of contributions from other types of interactions. A modification of this approach was suggested to take into account the effect of reorganization of an associated solvent.

In the previous paper [1], we examined the applicability of the LSER approach (linear solvation energy relationship) to describing the enthalpies of solvation of 183 organic nonelectrolytes in 36 solvents (a total of 1539 enthalpies of solvation). We considered three equations correlating the enthalpy of solvation of a compound A_i in a solvent S ($\Delta H_{\text{solv}}^{A_i/S}$) with the parameters of a solute:

$$\Delta H_{\text{solv}}^{A_i/S} = i + vV_x + s\pi_2^{\text{H}} + rR_2 + a\Sigma\alpha_2^{\text{H}} + b\Sigma\beta_2^{\text{H}}, \tag{1}$$

$$\Delta H_{\text{solv}}^{A_i/S} = i + l\log L^{16} + s\pi_2^{\text{H}} + d\delta_2 + a\Sigma\alpha_2^{\text{H}} + b\Sigma\beta_2^{\text{H}}, \tag{2}$$

$$\Delta H_{\text{solv}}^{A_i/S} = i + h\Delta H_{\text{solv}}^{A_i/\mathbf{I}} + s\pi_2^{\text{H}} + rR_2 + a\Sigma\alpha_2^{\text{H}} + b\Sigma\beta_2^{\text{H}}, \tag{3}$$

where V_x is the characteristic McGowan volume; $\log L^{16}$, the logarithm of the Ostwald coefficient, proportional to the free energy of solvation of compounds in hexadecane; and $\Delta H_{\text{solv}}^{A_i/\mathbf{I}}$, the enthalpy of solvation of compounds in cyclohexane (**I**). The terms vV_x, $l\log L^{16}$, and $h\Delta H_{\text{solv}}^{A_i/\mathbf{I}}$ reflect the energy of cavity formation in the solvent S to accommodate the solute molecule and the energy of general dispersion interaction between the solute and solvent. The parameter π_2^{H} is the measure of the polarity and polarizability of the solute [2, 3]; R_2 is the excess molecular refraction; $\Sigma\alpha_2^{\text{H}}$ and $\Sigma\beta_2^{\text{H}}$ are the effective acidity and basicity of solutes. The first three terms reflect the nonspecific solvation, and the next two terms, the specific solute–solvent interaction. We analyzed not only the quality of the resulting correlations, but also the interpretation of the parameters used and of the resulting terms. We restricted the consideration to the parameters related to nonspecific solvation.

In this work, the major attention will be focused on the terms $a\Sigma\alpha_2^{\text{H}}$ and $b\Sigma\beta_2^{\text{H}}$, which reflect the specific solute–solvent interaction.

The corresponding terms in Eqs. (1)–(3) have the same physical sense. Furthermore, as demonstrated in [1], these equations describe the experimental data with approximately equal accuracy. Therefore, in what follows, when analyzing the applicability of Eqs. (1)–(3), we will give only the results of the calculations by Eq. (3). The choice of just this equation is governed by the fact that, with this equation, the rms deviation is somewhat smaller [1].

Before analyzing the enthalpies of solvation, it seems necessary to give some definitions related to the enthalpy of specific interaction.

By the enthalpy of specific interaction of a solute A_i with a solvent S [$\Delta H_{\text{int}}^{A_i/S}$(sp.)] is meant the enthalpy of all the processes occurring when molecules A_i and S form a hydrogen bond or a charge-transfer complex. If a single complex species (e.g., 1 : 1) is formed in solution, then $\Delta H_{\text{int}}^{A_i/S}$(sp.) is related to the enthalpy of complexation ($A_i + S \rightleftarrows A_iS$), $\Delta H_{\text{c}}^{A_i/S}$, by

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[1] For communication I, see [1].

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$$\Delta H_{\text{int}}^{A_i/S}(\text{sp.}) = \alpha \Delta H_{\text{c}}^{A_i/S}. \qquad (4)$$

where α is the degree of complexation of A_i, varying fro 0 to 1.

All systems in which the solute specifically interacts with the solvent can be conventionally subdivided into four types. First type: there are no intramolecular hydrogen bonds in the solute (A_i) and solvent (S) molecules and no intermolecular solvent–solvent hydrogen bonds. Second type: there are no intramolecular hydrogen bonds in A_i and S molecules, but the solvent is associated via intermolecular hydrogen bonds. Third type: intramolecular hydrogen bonds in A_i molecules are formed, but intermolecular hydrogen bonds in the solvent are absent. Fourth type: both intramolecular hydrogen bonds in A_i and intermolecular hydrogen bonds in the solvent are present.

Since specific solute–solvent interactions often play a decisive role in various physicochemical processes, numerous approaches have been developed to separate the contribution made by specific interaction to the enthalpy of solvation. A comparative analysis of these approaches was made in [4–7], and recommendations were developed for correct quantitative determination of the enthalpy of specific solvation for the first three types of systems. Here we consider the first two types.

In this paper, by associated solvent we mean a solvent whose molecules are associated via hydrogen bonds.

Among all the solute parameters used in Eqs. (1)–(3), $\Sigma\,\alpha_2^H$ and $\Sigma\,\beta_2^H$ seem to be the most substantiated, since in most cases they were derived from the equilibrium constants of hydrogen bond formation between an acid and a base in carbon tetrachloride or in 1,1,1-trichloroethane. Nevertheless, certain problems arise with these parameters.

First, if multiparameter equations (1)–(3) are interpreted unambiguously, then, apparently, there is no need to assume (as it is made in [3, 8]) that $b = 0$ for solvents exhibiting no pronounced acid function. In this case, calculation by Eqs. (1)–(3) should give a zero or statistically insignificant value of b. We took advantage of our previous data [1]. The solvent parameters calculated by Eq. (3) are listed in Table 1. In this table, there are two rows for each solvent. Data taken from [1] are placed in the first row; these values were calculated "taking into account the nature of the solvent," e.g., the solvent could not be a proton donor and the term $b\Sigma\beta_2^H$ was eliminated. In calculations for alkanes and tetrachloromethane, both terms related to specific interaction were eliminated. The parameters given in the second raw were calculated by the full form of Eq. (3), "without taking into account the nature of the solvent." If Eq. (3) adequately reflects the contributions from various types of intermolecular interactions, it was natural to expect that it would take into account the nature of the solvent "automatically." This is indeed the case, but only for approximately a half of the solvents listed in the table. In the remaining cases, the results of calculations by Eq. (3) suggest occurrence of nonrealistic types of solvent–solute interaction. The statistically significant coefficients are printed bold in the last two columns of Table 1. The coefficients were considered statistically significant if the *p*-test for them exceeded 0.05.

At first glance, this drawback is insignificant, as in most cases the capability of a solvent to behave as an acid or a base can be predicted *a priori*. However, a question arises about the reliability of conclusions based on the *a* and *b* values for solvents that can act simultaneously as proton donors and proton acceptors, i.e., for solvents for which Eqs. (1)–(3) describing the thermodynamic parameters of solvation include all the six parameters. Is it possible to make conclusions on the relative proton-acceptor and proton-donor powers of such solvents, based on the parameters *a* and *b*? Among such solvents are alcohols, carboxylic acids, water, aniline, etc. It should be noted that the majority of studies using the LSER approach concern specifically associated solvents.

The second problem is that, in papers available to us, the correctness of using Eqs. (1) and (2) was not checked by comparing the terms of specific interaction ($a\Sigma\alpha_2^H$ and $b\Sigma\beta_2^H$) with data on the enthalpies or free energies of complexation, obtained either in CCl_4 by spectroscopic methods or in the neat base.

We will perform such an analysis in several steps. First, we consider proton-acceptor solvents with no solvent–solvent hydrogen bonding. Correct determination of the hydrogen bond energy is a sophisticated problem, and the results obtained by different authors sometimes disagree with each other. Therefore, we chose data for several extensively studied systems, with phenol, 1-butanol, and pyrrole as solutes. The enthalpies of specific interaction for these solutes, determined by Eq. (3) as the sum ($a\Sigma\alpha_2^H + b\Sigma\beta_2^H$), are listed in Table 2. These data are given in columns I. For comparison, in columns II we give the enthalpies of the specific interaction calculated by a somewhat modified procedure, consisting in the following. The enthalpy of solvation can be represented

Table 1. Parameters of Eq. (3) for calculating the enthalpies of solvation (kJ mol^{-1}) in some solvents “with” (first row) and “without” (second row) taking into account their chemical nature[a]

Solvent	*N*	*R*	S_0	*i*	*h*	*s*	*r*	*a*	*b*
Hexane	31	0.998	0.85	0.71±0.70	1.05±0.01	0.71±0.71	–0.15±0.63	–	–
	31	0.998	0.80	1.24±0.74	1.06±0.01	–0.76±1.04	0.45±0.68	**–3.94±1.85**	1.70±1.11
Heptane	38	0.998	0.82	0.75±0.46	1.06±0.01	0.95±0.61	–0.69±0.66	–	–
	38	0.998	0.77	0.95±0.47	1.06±0.01	0.61±0.82	–0.38±0.74	**–1.83±0.73**	0.79±0.80
Hexadecane	76	0.974	3.30	–0.42±0.92	1.00±0.03	–1.33±1.76	0.79±2.03	–	–
	76	0.981	2.92	0.39±0.84	1.03±0.03	–2.59±2.02	0.92±1.97	**–10.26±2.23**	**4.60±2.08**
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	–
	77	0.993	1.42	1.00±0.68	0.92±0.02	–11.17±0.97	0.71±0.75	–10.51±1.10	**–4.27±1.15**
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	–
	66	0.996	1.03	0.11±0.56	0.96±0.01	–12.33±0.74	3.12±0.58	–12.31±0.92	–0.65±0.81
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	–
	17	0.999	0.58	1.82±0.62	1.04±0.01	–16.88±1.47	7.48±0.94	–9.28±1.12	2.59±1.34
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	–
	36	0.996	1.18	0.80±0.80	1.03±0.02	–10.36±1.39	4.17±1.36	–14.39±1.34	0.15±1.34
Tetrachloromethane	76	0.992	1.41	–1.90±0.65	0.96±0.02	–8.54±0.63	2.33±0.59	–	–
	76	0.997	0.88	–0.67±0.45	0.97±0.01	–4.79±0.57	0.22±0.45	**–2.00±0.82**	**–5.97±0.63**
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	–
	17	0.999	0.74	1.34±0.89	0.99±0.02	–15.70±1.88	6.07±1.23	–9.24±2.02	**–2.35±0.82**
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	–
	33	0.996	1.12	0.10±0.79	0.94±0.02	–13.47±1.34	4.68±1.30	–5.55±1.47	**–4.29±1.32**
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	–
	38	0.966	2.11	3.99±1.66	0.81±0.04	–13.12±4.62	2.12±3.13	–34.91±5.83	**13.07±5.44**
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	–
	16	0.998	0.94	0.22±1.28	1.01±0.04	–11.76±1.62	3.46±1.53	–39.55±1.56	5.36±2.54
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	–
	33	0.995	1.34	–0.64±1.02	1.01±0.02	–6.03±1.52	1.42±1.43	–39.28±1.75	1.73±1.60
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	–
	21	0.995	1.64	2.24±1.53	0.98±0.03	–22.24±2.94	4.86±1.92	–34.92±2.01	**8.84±3.67**
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	–
	33	0.994	1.52	0.98±1.20	0.84±0.03	–16.84±2.40	0.21±1.47	–31.52±1.53	–2.65±2.28
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	–
	54	0.993	1.51	–1.40±0.91	0.84±0.02	–15.26±1.23	1.21±0.92	–35.44±1.37	–0.13±1.37
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	–
	15	0.999	0.79	2.71±0.80	0.94±0.02	–10.69±2.75	0.43±1.87	–31.49±2.56	**–10.25±3.45**
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	–
	37	0.976	3.28	2.95±2.38	1.09±0.05	1.64±3.43	–6.18±3.36	–58.02±2.99	–6.56±3.50
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	–
	21	0.995	1.38	3.59±1.41	0.95±0.03	–14.43±1.42	0.25±1.83	–20.26±1.56	–3.73±1.85
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	–
	24	0.998	0.87	0.11±0.84	0.91±0.02	–15.77±1.41	4.25±0.89	–28.24±1.58	–2.95±1.55
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	–
	77	0.991	1.88	1.09±0.86	0.80±0.02	–16.24±1.39	–2.01±1.04	–47.07±1.42	**–4.75±1.60**
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	0.989	1.92	1.05±1.82	0.92±0.06	–9.65±2.24	–0.57±1.69	–45.08±2.12	**–8.66±2.38**
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	–
	56	0.985	2.40	–0.01±1.59	0.66±0.04	–14.35±1.68	–5.40±1.43	–50.20±1.92	**–5.94±2.07**

[a] (*N*) Sample size, (*R*) correlation coefficient, and (S_0) rms deviation of the calculated enthalpies of solvation from the experiment.

Table 2. Enthalpies of specific interaction of phenol, 1-butanol, and pyrrole with various solvents, kJ mol^{-1}, at 298 K[a]

Solvent	Phenol			1-Butanol			Pyrrole		
	I	II	III	I	II	III	I	II	III
Benzene	–6.3	–6.6	–4.9,[b] –6.5[b]	–4.6	–4.1	–0.8,[c] –2.1[b]	–6.2	–4.5	
Toluene	–6.3	–7.5	–6.9,[b] –5.6[b]	–3.7	–4.6	–2.1[b]	–5.3	–5.1	
p-Xylene	–5.0	–5.4	–8.7[b]	–	–3.3	–	–	–	
Mesitylene	–7.7	–8.6	–6.6,[b] –8.0[b]	–	–5.3	–2.3[b]	–	–	
Dipropyl ether	–23.6	–22.9	17.6,[b] –22.5[d]	–13.0	–14.1	–12.3[b]	–13.7	–15.7	–10.3[c]
THF	–24.3	–20.1	–22.6,[c] –23.0[e]	–	–12.4	–12.8[d]	–14.8	–13.8	–11.7[c]
1,4-Dioxane	–20.5	–19.1	–19.2,[c] –20.9,[b] –22.0[b]	–14.4	–11.8	–11.7,[f] –13.0[b]	–13.5	–13.1	–9.2[c]
Ethyl acetate	–20.6	–21.3	–18.4,[c] –17.6,[b] –20.2[b]	–12.6	–13.1	–9.2,[c] –10.2[b]	–12.3	–14.5	–7.9[c]
Acetone	–23.0	–22.0	–20.9,[c] –20.1[b]	–14.9	–14.9	–10.0,[c] –9.2[b]	–	–	–
Triethylamine	–	–	–	–26.3	–21.7	–23.1[b]	–22.6	–24.1	
Acetonitrile	–16.1	–18.4	–15.5,[c] –16.4[b]	–9.9		–7.1[c]	–11.0	–13.3	–7.1,[c] –7.9[g]
Benzonitrile	–	–	–	–	–	–	–10.6	–12.4	
DMF	–28.9	–28.8	26.8,[c] –25.5[b]	–19.7	–17.8	–15.1,[c] –17.3[b]	–16.8	–19.7	–10.3
Pyridine	–31.1	–28.6	–30.4,[c] –29.3[b]	–20.5	–17.7	–17.6,[c] –20.9[b]	–17.3	–19.6	–13.4
DMSO	–29.2	–30.9	–28.5,[c] –30.17[b]	–20.6	–19.1	–15.9[c]	–19.0	–21.1	–16.3

[a] (I) Values calculated by Eq. (3) as the sum $a\sum\alpha_2^H + b\sum\beta_2^H$; (II) calculated by the method of base compounds; (III) published data on the enthalpies of specific interaction. [b] Data of [9]. [c] Data of [4]. [d] Data of [10]. [e] Data of [11]. [f] Data of [12]. [g] Data of [13].

as the sum of the enthalpies of nonspecific solvation and specific interaction. In this case, the enthalpy of specific interaction can be determined by Eq. (5):

$$\Delta H_{\text{int}}^{\text{A}_i/\text{S}}(\text{sp.}) = \Delta H_{\text{solv}}^{\text{A}_i/\text{S}} - \Delta H_{\text{solv}}^{\text{A}_i/\text{S}}(\text{nonsp.}). \qquad (5)$$

Since the enthalpy of specific solvation is described by the last two summands in Eq. (3), the enthalpy of nonspecific solvation will be determined by

$$\Delta H_{\text{solv}}^{\text{A}_i/\text{S}}(\text{nonsp.}) = i + h\Delta H_{\text{solv}}^{\text{A}_i/\mathbf{I}} + s\pi_2^{\text{H}} + rR_2. \quad (6)$$

The parameters *i*, *h*, *r*, and *s* in Eq. (6) for each proton-acceptor nonassociated solvent were obtained from the experimentally determined enthalpies of solvation for “base” compounds, i.e., for solutes showing no proton-donor properties. With the resulting equations, using the known data on $\Delta H_{\text{solv}}^{\text{A}_i/\mathbf{I}}$, R_2, and π_2^{H} for phenol, 1-butanol, and pyrrole, we calculated $\Delta H_{\text{solv}}^{\text{A}_i/\text{S}}(\text{nonsp.})$. Then, using Eq. (5), we determined the enthalpies of specific interaction of these compounds with the solvent.

In columns III of Table 2, we give the published enthalpies of specific interaction. These data were obtained by spectral and calorimetric methods.

On the whole, although the enthalpies of specific solute–solvent interactions were determined using different approaches, they are in reasonable agreement. This fact means that Eq. (3) allows adequate determination of the enthalpy of specific interaction in nonassociated aprotic solvents.

In contrast to nonassociated solvents, formation of hydrogen bonds of a solute with an associated solvent can generally involve cleavage of hydrogen bonds between solvent molecules. Correspondingly, the enthalpy of specific interaction with an associated solvent will depend in a complex manner on the solvent association and on structural features of solute molecules [5]. These two factors determine the energy required to shift the association equilibrium in the solvent at formation of solute–solvent complexes (solvent reorganization energy). Previously, based on studies of solvation enthalpies in associated solvents, we developed an approach allowing qualitative conclusions on the occurrence (or absence) of the solvent reorganization effect in formation of solute–solvent complexes [5]. This approach consists in comparing the numbers of lone electron pairs capable of hydrogen bonding and of active hydrogen atoms in the solvent molecule. The type of hydrogen bonding centers (active hydrogen atoms or lone electron pairs) present in excess determines the type of solutes with which the solvent reorganization energy should be manifested at specific interaction. For example, in alcohols as solvents, the number of lone electron pairs

Table 3. Enthalpies of specific interaction of solutes with methanol (kJ mol^{-1}, 298 K), calculated by various procedures^{a}

Solute	I	II	III	IV	Solute	I	II	III	IV
Dichloromethane	–4.89	–2.45		–4.42	Cyclohexanone	–11.60	–0.41		–5.46
Chloroform	–6.19	–5.50		–6.63	3,3-Dimethylbutanone	–10.56	–0.43		–2.43
Water	–38.82	–31.86		–36.26	Benzaldehyde	–8.08	–0.21		0.00
Methanol	–26.29	–19.60		–19.01	Acetophenone	–10.15	1.48	–8.0^{b}	–1.21
Ethanol	–24.19	–19.75		–16.97	Butylamine	–18.79	–21.32		–15.57
1-Propanol	–24.19	–22.80		–16.97	Diethylamine	–17.16	–18.49		–16.28
1-Pentanol	–24.19	–20.29		–16.97	Dibutylamine	–17.16	–18.85		–16.28
2-Methyl-2-butanol	–24.36	–26.25		–21.60	Diisopropylamine	–17.78	–20.56		–18.10
Phenol	–29.52	–23.02		–26.53	Triethylamine	–16.36	–16.83	–24.9,^{b}	–19.42
m-Cresol	–28.99	–25.32		–25.21				–15.9^{c}	
Diethyl ether	–9.32	–2.23	–12.0,^{b}	0.00	Aniline	–20.37	–11.45		–13.32
			–15.6^{c}		*N*-Methylaniline	–15.45	–4.83		–7.52
tert-Butyl methyl ether	–9.32	–7.58		0.00	*N*,*N*-Dimethylaniline	–8.70	1.80	–8.5^{c}	0.00
					Nitromethane	–8.94	–1.86		–2.65
Anisole	–6.01	0.32	–7.1^{c}	0.00	Nitroethane	–7.60	0.34		–0.88
Ethyl benzoate	–9.53	2.63		0.00	Acetonitrile	–8.37	0.83	–9.2,^{c}	–1.77
Acetone	–12.10	–0.09	–10.0,^{d}	–4.20				–3.8^{c}	
			–15.1^{c}		Propionitrile	–8.23	1.09		–0.88
Butanone	–10.56	0.57		–2.43	Butyronitrile	–7.46	2.32		0.00
2-Pentanone	–10.56	0.59		–2.43	Benzonitrile	–6.83	1.60	–5.0^{b}	0.00
3-Pentanone	–10.56	0.08	–14.2^{c}	–2.43	DMF	–15.12	–0.32	–14.6,^{b}	–15.78
2-Hexanone	–10.56	0.53		–2.43				–15.5^{c}	
2-Heptanone	–10.56	0.04		–2.43	Pyrrole	–21.79	–11.14		–18.13
4-Heptanone	–10.56	–0.23		–2.43	Pyridine	–10.77	–5.52	–16.3,^{d}	–3.03
2-Octanone	–10.56	–0.06		–2.43				–13.4^{c}	
2-Nonanone	–10.56	0.24		–2.43	2-Methylpyridine	–11.80	–7.91		–6.07
5-Nonanone	–10.56	–0.04		–2.43	4-Methylpyridine	–11.39	–7.19		–4.85
2-Decanone	–10.56	–1.06		–2.43	2,6-Dimethylpyridine	–12.84	–9.62	–16.7,^{c}	–9.10
2-Undecanone	–10.56	–1.12		–2.43				–20.9^{c}	
Cyclopentanone	–10.77	1.48		–3.03	Quinoline	–11.18	–6.03	–15.9^{b}	–4.25

^{a} (I) Eq. (3), (II) Eqs. (5) and (7), (III) published data, and (IV) Eq. (8). ^{b} Data of [10]. ^{c} Data of [9]. ^{d} Data of [4].

is twice that of active hydrogen atoms. This means that solutes specifically interacting with a solvent via lone electron pairs (ketones, ethers, esters) should cause reorganization of an alcohol as solvent. With proton-donor solutes, e.g., chloroform, the solvent reorganization should not be manifested. If the numbers of lone electron pairs and active hydrogen atoms are equal, the solvent reorganization should be manifested at solvation of both proton donors and proton acceptors.

Does Eq. (3) take into account such a complex pattern in describing the enthalpy of specific interaction of a solute with an associated solvent? To answer this question, let us analyze data on the enthalpies of solvation of various compounds in methanol, because for this associated solvent the available experimental data on the enthalpies of solvation are the most extensive.

We analyzed the applicability of Eqs. (3) and (6) to describing the enthalpies of solvation of various compounds in methanol. The solute parameters π_2^H, R_2, $\Sigma\,\alpha_2^H$, and $\Sigma\,\beta_2^H$ were taken from [8, 14, 15], and the enthalpies of solvation of various compounds, from [1, 4, 10, 16–41]. A total of 88 solutes are considered, including diverse nonelectrolytes such as linear and branched alkanes, alkenes, aromatic hydrocarbons, their halo derivatives, alcohols, phenols, ethers, esters, ketones, amines, nitro compounds, etc. Analysis was performed similarly to that made for nonassociated solvents. First, we determined the enthalpies of specific interaction with methanol by Eq. (3) as the sum $a\Sigma\,\alpha_2^H + b\Sigma\,\beta_2^H$. The results are given in Table 3, column I. The parameters of Eq. (3) for methanol are given in [1] (*a* –38.50, *b* –20.71). In column II are given the enthalpies of specific interaction calculated by Eqs. (5) and (6). As "base" solutes for calculating the enthalpy of nonspecific solvation by Eq. (6), we chose solutes that do not form hydrogen bonds with the solvent, i.e., the "base" compounds did not include proton donors (hydroxy compounds, chloroform), amines, pyridines, and ketones. It should be noted, however, that some of the "base" compounds (e.g., benzene, nitrobenzene) are potentially capable of hydrogen bonding with methanol. However, such hydrogen bonds are too weak to break methanol–methanol hydrogen bonds in the course of dissolution. From data for "base" compounds, we calculated *i*, *h*, *s*, and *r* by a multiple linear regression procedure. As a result, Eq. (6) for methanol takes the following form:

$$\Delta H_{\text{solv}}^{\text{A}_i/\text{CH}_3\text{OH}}(\text{nonsp.}) = -0.92 + 0.83\Delta H_{\text{solv}}^{\text{A}_i/\mathbf{I}} - 14.4\pi_2^{\text{H}} + 1.30R_2. \tag{7}$$

The enthalpies of specific interaction with methanol, calculated by Eqs. (5) and (7), are listed in Table 3, column II.

If Eq. (3) describes the enthalpies of specific interaction of solutes with methanol adequately, the quantities in columns I and II should coincide. As seen from Table 3, for the majority of proton acceptors this is not the case. With pyridine, occasional coincidence, in our opinion, is caused by unduly low value of $\Sigma\,\beta_2^{\text{H}}$ for this compound (0.52), i.e., the "basicity" of pyridine is assumed to be equal to that of ketones. It should be noted that, in [3], $\Sigma\,\beta_2^{\text{H}}$ of pyridine is taken to be 0.90, which seems to be a more realistic value. With this value, the data in columns I and II will differ significantly. As for proton-donor compounds exhibiting a weak basic function (phenol, *m*-cresol, chloroform), the enthalpies of their specific interaction calculated by the two procedures coincide.

In contrast to proton acceptors, proton donors do not cause reorganization of the solvent (aliphatic alcohol) [5]; therefore, with respect to these compounds the solvent behaves like a nonassociated proton acceptor. In this respect, data for aniline, *N*-methylaniline, and *N*,*N*-dimethylaniline are worth noting. As active hydrogen atoms are substituted, the relative difference between the values in columns I and II increases, but the absolute difference is approximately constant. This fact suggests that the enthalpy of solution of aniline in methanol is governed by the proton-donor power of aniline, whereas its proton-acceptor power is not manifested because of the solvent reorganization.

For some compounds, enthalpies of formation of a hydrogen bond with methanol are available from the literature. These data are given in column III of Table 3. They are better consistent with the values in column I than with those in column II. This is quite natural, as the published data were determined either in an inert solvent (tetrachloromethane) or in the neat proton acceptor. In both cases, structural reorganization of the solvent exerts no effect. However, it should be noted that, for strong proton acceptors (aliphatic amines, pyridine, quinoline), the enthalpies of specific interaction calculated by Eq. (3) (column I) are appreciably underestimated as compared to published data. The reason for this is as follows. If the contribution of all proton acceptors to the enthalpy of specific interaction were zero, then calculation by Eq. (3) would give the zero value for *b*. However, strong proton acceptors can break the methanol–methanol hydrogen bond. Specifically these compounds are responsible for the nonzero (–20.71) value of *b* calculated by Eq. (3). However, this value is a certain mean depending on the ratio of strong and weak proton acceptors in the sample. As a result, the enthalpies of specific interaction calculated by Eq. (3) (column I) are overestimated for weak and underestimated for strong proton acceptors. Thus, the effect of reorganization of the solvent structure contributes to the enthalpies of solvation of strong proton acceptors also (a comparison of columns I and II only could erroneously lead to an opposite conclusion). On the whole, Eq. (3) does not reflect adequately such an important phenomenon as reorganization of the structure of an associated solvent at formation of hydrogen bonds with a solute.

We propose the following mechanism to take into account, to a first approximation, the effect of the solvent reorganization. Modified Eq. (3) for methanol will have the following form:

$$\Delta H_{\text{solv}}^{\text{A}_i/\text{S}} = i + h\Delta H_{\text{solv}}^{\text{A}_i/\mathbf{I}} + s\pi_2^{\text{H}} + rR_2 + a\Sigma\alpha_2^{\text{H}} + b\beta'. \tag{8}$$

This equation differs from (3) in the parameter β' characterizing the proton-acceptor power of the solute (naturally, the values of *i*, *h*, *s*, *r*, *a*, and *b* in this case will be different). The parameter β' is determined by the difference between the parameters $\Sigma\,\beta_2^{\text{H}}$ for a given solute and methanol. If $\Sigma\,\beta_2^{\text{H}}$ of a given solute is lower than that of methanol, β' = 0. For other compounds, β' is equal to the difference between these parameters.

Correspondingly, the enthalpy of specific interaction with methanol will be equal to the sum $a\Sigma\alpha_2^H + b\beta'$. The multiple linear regression procedure applied to Eq. (8) gives for a and b the values of -44.2 and -60.7, respectively. The enthalpies of specific interaction calculated by Eq. (8) are listed in column IV of Table 3. It is seen that the agreement between data in columns IV and II is considerably better than between data in columns I and II. However, full coincidence is not attained, because, firstly, Eq. (8) is only a first approximation in estimating the reorganization effect and, secondly, the error in detemining the difference between the parameters $\Sigma\beta_2^H$ for two compounds is considerably larger than the error of each of these parameters. For example, if we assume that $\Sigma\beta_2^H$ for pyridine is underestimated by 5%, then β' for pyridine will be underestimated by 52%. However, this fact may be an advantage of Eq. (8) rather than its drawback, as this equation can be a sensitive tool for testing the reliability of the parameters $\Sigma\beta_2^H$ for various solutes.

The analysis made by us in the previous paper [1] and in this work allows the following conclusions.

(1) LSER equations satisfactorily describe the enthalpies of solvation of a large set of organic nonelectrolytes in various media. However, because of the LSER approach being formal, the conclusions concerning contributions of various types of intermolecular interactions to the enthalpy of nonspecific solvation are contradictory.

(2) LSER equations satisfactorily reflect the contribution of specific interaction of a solute with nonassociated proton-acceptor solvents to the enthalpy of solvation. However, they incorrectly reflect the contribution of specific interaction to the enthalpy of solvation in associated solvents. This means that the satisfactory description of the enthalpies of solvation, observed in many cases, is an occasional result of averaging and redistribution of contributions from other types of interactions. A modification of multiparameter linear equations was proposed to take into account, to a first approximation, the effect of reorganization of an associated solvent at its specific interaction with a solute.

EXPERIMENTAL

The experimental enthalpies of solvation used in calculations were determined as differences between the published values of the enthalpies of solution [1, 4, 10, 16–41] and vaporization [42, 43]. If several contradicting values were available, we preferred the values obtained calorimetrically, or those obtained in more recent studies.

Table 4. Coefficients of mutual correlation of solute parameters used simultaneously in Eqs. (3), (6), and (8)

Parameter	$\Delta H_{solv}^{A_i/\mathbf{I}}$	π_2^H	R_2	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	β'
$\Delta H_{solv}^{A_i/\mathbf{I}}$	1.000	–0.076	–0.271	0.369	0.095	0.004
π_2^H	–0.076	1.000	0.641	0.058	0.459	0.040
R_2	–0.271	0.641	1.000	0.026	–0.024	–0.157
$\Sigma\alpha_2^H$	0.369	0.058	0.026	1.000	0.177	–
$\Sigma\beta_2^H$	0.095	0.459	–0.024	0.177	1.000	–
β'	0.004	0.040	–0.157	–	–	1.000

Statistical calculations by Eqs. (3), (6), and (8) were performed by the multiple linear regression procedure using the Statistica software. In LSER calculations, mutual correlation of solute parameters is unadmissible. The coefficients of mutual correlation of the solute parameters are listed in Table 4. It is seen that noticeable correlation is observed only between the parameters π_2^H and R_2 (0.641). However, in our opinion, a certain correlation between the parameters does not make the corresponding equations unsuitable for calculating the enthalpies of solvation; it only brings about certain indefiniteness in the resulting solvent parameters (in this case, s and r). From the viewpoint of physical sense of these linear correlations, it is significant that the new parameter β' does not correlate with any of the other simultaneously used parameters.

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