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Energetic characteristics of solvation in the solutions of polar organic compounds

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Abstract

The present paper carries the analysis of various contributions into the total energy of intermolecular interaction (IMI) ΔU_S in infinitely diluted solutions, that are formed by aliphatic (including alcohols) and aromatic polar compounds with polar and non-polar, associated and non-associated solvents at 298 K.

The calculation within the frames of the earlier suggested continuum method of IMI energy and of its separate constituents in the systems studied is carried out, and the cases of their deviations from experimentally determined analogues are analyzed to resolve the above task. Compounds are distinguished for which there is a strengthening or weakening of the energy of the hydrogen bond between the molecules of solute and solvent in solution, if compared with the analogous value between the individual liquid molecules. Quantitative values of the energetic expenditure for the destruction of associative bonds in solvents upon formation of solutions are estimated.

INTRODUCTION

The problem of the quantitative description of the energetics of intermolecular interactions in liquids and solutions within the frames of different approaches (discrete, continuum) remains despite all the efforts made to resolve it. The present paper continues logically our series of works [1–4] aimed at the resolution of this task within the framework of the continuum approach, which is based on the theory of polarization of dielectrics. This paper carries the analysis of various contributions to the total energy of intermolecular interactions (IMI) ΔU_S in infinitely dilute solutions, which are formed by aliphatic including alcohols and aromatic polar compounds with polar and non-polar, associated and non-associated solvents at 298 K.

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METHOD

To resolve the task given, the calculation of IMI energy ΔH_S and of its separate constituents in the systems studied is carried out within the framework of the continuum method suggested earlier [1–4], and the cases of their deviation from experimentally determined analogues are analyzed. The expressions for determining ΔH_S, according to refs. 1–4 have the form

$$\Delta U_S = \Delta U_{o-i} + \Delta U_{disp} = \Delta F_{o-i} + T\Delta S_{o-i} + \Delta U_{disp} \qquad (1)$$

$$\Delta U_{o-i} = -\frac{\mu_A^2}{a_{o-i}^3}\frac{(\lambda_A+2)(\varepsilon_B-1)N_A}{(2\varepsilon_B+\lambda_A)3} - \frac{\mu_A^2}{a_{o-i}^3}\frac{(\lambda_A+2)^2\varepsilon_B(2\varepsilon_B+n_B^2)(\varepsilon_B-n_B^2)N_A}{(2\varepsilon_B^2+n_B^4)(2\varepsilon_B+\lambda_A)^2 3} \qquad (2)$$

$$\Delta U_{hy(o-i)} = \frac{3}{2}\frac{\hbar e^{1/2}}{m_e^{1/2}}\frac{(N_e/\bar{\alpha})_{A,eff}^{1/2}(N_e/\bar{\alpha})_{B,eff}}{(N_e/\bar{\alpha})_{A,eff}^{1/2}+(N_e/\bar{\alpha})_{B,eff}^{1/2}}\left(\frac{\bar{\alpha}}{r_{str}^3}\right)\frac{(n_B^2-1)}{(n_B^2+2)} \qquad (3)$$

Here $-\Delta U_S$ is the change in the internal energy of the solution at switching off of IMI of molecule A with the solvation shell made of molecules B for the case of N_A not interacting with other solvate molecules. The analysis carried out in refs. 2 and 3 allows us to establish that the contribution of ΔU_{o-i} to ΔU_S is determined by the coulombic, polarization IMIs. It also includes the short-range IMIs, that are conditioned by the attraction and repulsion forces; ΔU_{disp} reflects the contribution from the dispersion-nature attraction forces that are independent of orientation, and also from the repulsion forces that are conditioned by the exchange interactions. It is noteworthy that the possibility of ΔU_{disp} determination using the comparatively simple correlation (3) relates to the above-mentioned property of ΔU_{o-i} to take into account, within the framework of the approach given, all types of IMI that are dependent on the orientation of molecules within the solvate: μ_A, $\bar{\alpha}$, a_{o-i} are the dipole moment of the molecule dissolved in gaseous phase, average polarizability and effective radius of the orientation-induction IMIs, respectively, which make up the microcharacteristics of the dissolved molecule [5–7].

$$\lambda_A^3 = (2\bar{\alpha}/r_{str}^3 + 1)/(1 - \bar{\alpha}/r_{str}^3)$$

ε_B and n_B are the dielectric permeability and solvent refraction index, respectively; $(N_e/\bar{\alpha})_{eff}^{1/2}$ is the molecular parameter, the method of determination of which is given elsewhere [1]; r_{str}^3 is the volume per molecule of liquid. The micro- and macro-characteristics of the compounds considered that are necessary to calculate ΔU_S, as well as the electrooptical parameters of solvents taken from refs. 1–4 and 8, are shown in Table 1.

As before [1–4], the value of ΔU_{exp} given by eqn. (4) was used as the

TABLE 1

Physicochemical properties of the solvents used at 298 K

No.[a]	Solvent	$a^3_{o-i} \times 10^{-24}$/ cm^3	$r^3_{str} \times 10^{-24}$/ cm^3	μ/D	ε	n	ΔH_{evap}/ kJ mol^{-1}	$(N_e/\alpha)^{1/2}_{eff}$ $\times{}^{-12}$/ cm$^{3/2}$
1	Heptane	0.0	58.0	0.00	1.924	1.3876	36.55	1.646
2	Hexane	0.0	52.1	0.00	2.023	1.3723	31.55	1.513
3	1,4-Dioxane	0.0	33.9	0.45	2.210	1.4200	35.70	1.392
4	Tetrachlormethane	0.0	38.4	0.00	2.238	1.4574	32.40	1.083
5	Toluene	46.4	42.3	0.36	2.379	1.4969	37.99	1.112
6	Mesitylene	0.0	55.2	0.00	2.274	1.4968	47.48	1.406
7	Benzene	0.0	25.7	0.00	2.275	1.4979	33.85	9.824
8	Triethylamine	43.1	55.4	0.66	2.420	1.4010	35.00	1.476
9	Dibutyl ester	64.4	67.4	1.22	3.060	1.3968	36.90	1.581
10	Chloroform	26.1	37.6	1.15	4.900	1.4429	32.20	1.106
11	Ethyl acetate	44.9	39.0	1.88	6.020	1.3698	35.10	1.644
12	Tetrahydrofuran	30.9	32.3	1.75	7.580	1.4050	32.00	1.242
13	Quinoline	56.6	46.9	2.18	9.000	1.6228	64.10	1.282
14	1,1-Dichloroethane	28.9	33.5	1.98	10.00	1.4138	31.00	1.121
15	1-Octanol	22.4	62.7	1.76	10.34	1.4275	72.00	2.693
16	Pyridine	38.0	32.0	2.37	12.30	1.5095	40.40	1.047
17	1-Hexanol	14.4	49.5	1.64	13.30	1.4161	61.90	2.360
18	2-Butanone	32.5	35.7	2.76	15.45	1.3764	34.10	1.387
19	1-Pentanol	14.5	43.0	1.70	13.90	1.4079	56.94	2.219
20	1-Butanol	11.5	36.4	1.75	17.90	1.3990	52.47	2.047
21	1-Propanol	30.7	29.7	3.09	20.33	1.3837	47.32	1.904
22	Acetane	21.9	29.3	2.69	20.82	1.3588	30.80	1.232
23	Ethanol	7.0	23.2	1.66	24.55	1.3594	42.30	1.787
24	Methanol	5.4	16.1	2.87	32.70	1.3265	37.43	1.624
25	Nitrobenzene	38.0	59.1	4.03	34.82	1.5500	52.50	1.072
26	Nitromethane	22.4	21.3	3.56	35.80	1.3796	38.30	1.252
27	Dimethylformamide	27.6	30.6	3.86	36.71	1.4282	47.50	1.383
28	Acetonitril	18.9	20.9	3.44	37.50	1.3416	33.20	1.158
29	*N*,*N*-Dimethylacetamide	24.8	36.8	3.69	37.78	1.4356	53.10	1.549
30	Dimethylsulphoxide	23.6	28.2	3.90	46.68	1.4773	52.90	1.240
31	Propylene carbonate	25.2	33.5	4.98	65.10	1.4189	49.79	1.166
32	Water	2.4	7.2	1.83	78.39	1.3325	43.99	1.046
33	Formamide	6.7	15.8	3.37	111.0	1.4173	65.00	1.215

[a] Enumeration of solvents in Tables 2 and 3 coincides with that in Table 1.

experimental analogue of ΔU_S

$$\Delta U_{exp} = \Delta U_{soln} - \Delta U_{evap,A} - \Delta U_{cav,A} \tag{4}$$

where ΔU_{soln} is the change in the internal energy of dissolution at infinite dilution; $\Delta U_{evap,A} \approx \Delta H_{evap,A} - RT$ is the change in the internal energy of a mole of substance A upon evaporation; $\Delta U_{cav,A} \approx \Delta H_{cav,A} - RT$ is the change in the internal energy of solvent upon cavity formation in it. It is noteworthy, that taking into account a small value of the volumetric effect of formation of the solution, one can state with a high degree of precision for solutions that $\Delta U_{soln} = \Delta H_{soln}$ [9]. For all the solutions considered, we used the values of ΔH_{soln} published elsewhere [10–29]. Of all the terms in eqn. (4), it is ΔU_{cav} that is the most difficult to determine. Unfortunately, not all methods of calculating this value yield results which are in agreement; here we should mention the Scaled Particle Theory [30–37], the theory of Sinanoglu [38–40] using the concept of surface tension. Furthermore, ΔU_{exp} loses its experimental sense where using these methods. Taking this into account, it is considered in the present paper that as in refs. 41–44, the ΔU_{evap} value (the change in the internal energy of a mole of solvent B at evaporation) is more correct than ΔU_{cav}.

RESULTS AND DISCUSSION

Table 2 shows values of ΔU_S calculated according to eqns. (1)–(3) and experimentally determined. The table shows that there is a satisfactory agreement between ΔU_S and ΔU_{exp} for the majority of solutions having different IMI characteristics; this confirms the correctness of the approach used. Here, the values of ΔU_S change over a side range ($56.6 \leqslant \Delta U_S \leqslant 114.5$ kJ mol^{-1}). It is noteworthy that the coincidence between the energies compared occurs for solutions of the compounds studied over a series of solvents with substantially different values of the molar volumes ($21.3 \leqslant r_{\text{str}}^3 \leqslant 56.7 \times 10^{-24}$ cm^3) and heats of evaporation ($45.5 \leqslant \Delta H_{\text{evap}} \leqslant$ 77.7 kJ mol^{-1}).

Considerable changes in various solutions are experienced, as shown by the values of the separate contributions $\Delta H_{\text{o-i}}$ and ΔU_{disp} to ΔU_S. In the case of non-polar solvent solutions $\Delta U_{\text{o-i}}$ is conditioned only by the induction IMIs, and in this connection, is much lower in magnitude than ΔU_{disp}. However, with increasing polarity of the medium, one can observe an increase in the contribution of $\Delta U_{\text{o-i}}$ up to magnitudes that are comparable with ΔU_{disp}. If this factor is not taken into account, it would have resulted in a disagreement between ΔU_S and ΔU_{exp}. Since the $\Delta U_{\text{o-i}}$ contribution is proportional to the dipole moment μ (see eqn. (2)), conclusions [45–48] about the absence of its influence on the solvation characteristics in solutions of polar compounds give rise to certain doubts.

When interpreting the correlation dependences of ΔU_S on the molecular refraction of solute R, Solomonov and co-workers [45–48] were obviously deluded by the two circumstances that are clearly reflected in Table 2. Firstly, the ΔU_{disp} contribution determined predominantly by dispersion IMIs tends to decrease in value with increasing polarity of solute and solvent (and consequently with increasing $\Delta U_{\text{o-i}}$ contribution). Thus, there is a change in the "weight" of each contribution ΔU_S in the solvents with different ε and n, the resulting ΔU_S value being, in principle, the same. Secondly, the increase in $\Delta U_{\text{o-i}}$ values for the solvents considered (see Table 2) with the change in their dielectric properties is of non-linear character. Indeed, as Table 2 shows, for each of the compounds considered, ΔH_{o-i} values become nearly twice as great upon transition from the solutions in hexane ($\varepsilon = 2.1$) to those in ethyl acetate ($\varepsilon = 6.02$). The further substantial increase in the dielectric permeability of solvents ($6.02 \leqslant \varepsilon \leqslant 100.1$) does not result in a noticeable change in the magnitude of this contribution.

When analysing in detail the data given in Table 2, it is of certain interest to consider the reasons for the systematic deviations of ΔU_S from ΔU_{exp}

TABLE 2

Calculated and experimentally determined IMI energies (in kJ mol^{-1}) for solutions of aromatic and aliphatic polar compounds at 298 K

	I. Quinoline			II. Pyridine			III. Benzaldehyde			IV. Nitrobenzene		
No.	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$
1	2.5	92.1		3.4	70.6		4.4	67.8		7.6	80.3	73.9
2	2.6	85.7	82.8	3.5	66.1	58.8	4.5	63.8		7.9	75.6	67.5
3	2.7	91.8		3.7	71.0		4.8	68.8	70.3	8.5	81.3	
4	2.7	87.1	89.6	3.7	68.3	66.3	4.9	66.9	63.7	8.6	78.3	75.3
5	2.8	94.7		3.9	74.2		5.1	72.6	71.8	9.0	84.9	
6	2.7	106.4		3.8	82.1		4.9	66.9		8.7	93.4	
7	2.7	88.6		3.8	69.9		4.9	68.7	67.7	8.7	80.0	79.3
8	2.8	90.7		3.9	70.2		5.1	68.0		9.1	80.8	78.4
9	3.1	93.0		4.5	72.0		5.9	69.8		10.7	83.7	80.4
10	3.7	86.7		5.4	68.8		7.2	68.1		13.4	81.9	81.9
11	3.9	89.8		5.7	70.0		7.7	68.5	68.9	14.4	84.1	83.6
12	4.1	85.6		6.0	67.9		8.2	67.4	68.7	15.4	82.3	
13	4.3	123.9	125.7	6.2	97.1		8.6	95.3		16.1	114.3	
14	4.3	83.0		6.4	66.4		8.7	66.4		16.4	81.3	78.1
15	4.4	122.5		6.4	93.0		8.8	89.1		16.5	110.5	110.9
16	4.5	95.4		6.6	76.3	75.8	9.0	76.1	75.0	17.0	92.3	87.9
17	4.5	114.8	121.9	6.6	87.9	97.4	9.1			17.3	105.4	103.4
18	4.6	85.2		6.8	67.7		9.3			17.6	83.5	
19	4.5	110.5		6.7	85.0		9.2			17.8	102.3	
20	4.7	105.4		6.9	81.6		9.5	79.4		17.9	98.9	
21	4.7	99.2		6.9	77.3		9.6	75.6		18.2	94.4	
22	4.7	77.4		7.0	62.2		9.6	62.4	64.6	18.2	77.9	78.3
23	4.8	91.5		7.1	71.8		9.8	70.7		18.5	88.6	85.1
24	4.9	81.1	99.6	7.2	64.3	77.0	9.9	63.9		18.9	80.7	80.8
25	4.9	103.7		6.9	77.3		9.6	75.6		18.2	94.4	
26	4.9	82.1		7.2	65.8		10.0	66.0		19.0	82.3	82.2
27	4.9	95.3		7.2	75.5		10.0	75.0	83.4	19.0	92.9	95.9
28	4.9	72.2		7.2	58.5		10.0	59.1	66.2	19.0	74.4	79.1
29	4.9	103.1		7.2	82.5		10.0	82.4		19.0	100.2	
30	5.0	99.0		7.3	78.8		10.1	78.5	86.3	19.2	96.6	97.5
31	5.0	86.2		7.4	69.3		10.2	69.6		19.5	86.4	
32	5.0	67.1		7.4	54.9		10.3	56.0		19.6	70.9	
33	5.1	87.8		7.5	70.4		10.4	70.6		19.7	87.8	

TABLE 2 (continued)

No.	V. Methanol			VI. 1-Propanol			VII. Pentanol			VIII. 1-Octanol		
	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$
1	9.0	66.8	53.2	5.7	78.2		4.1	86.2	65.9	3.2	95.9	79.3
2	9.4	62.8		5.9	72.6		4.2	79.5		3.3	88.0	
3	10.1	67.0		6.3	77.2		4.5	84.2		3.5	92.8	78.7
4	10.2	63.2	46.9	6.3	71.8	57.2	4.5	77.5	65.4	3.5	84.4	87.3
5	10.6	68.6		6.6	78.2		4.7	84.6	73.3	3.7	92.2	96.7
6	10.3	76.6		6.4	89.0		4.6	97.5	83.3	3.6	107.7	81.8
7	10.3	64.0	52.9	6.4	72.4		4.6	78.0	68.3	3.6	84.5	106.2
8	10.8	67.2		6.7	77.1		4.8	84.1	91.3	3.7	92.8	94.9
9	12.5	70.4		7.7	80.2		5.4	87.3	80.6	4.2	96.4	
10	15.5	67.7	56.3	9.4	73.9		6.5	78.5		5.0	84.7	
11	16.5	71.9	61.9	10.1	79.5		7.0	85.6	77.7	5.2	94.0	90.0
12	17.6	69.2		10.7	74.7		7.4	79.1		5.5	85.5	
13	18.2	94.4	99.2	11.1	105.6		7.6	113.6		5.7	123.9	
14	18.6	68.1		11.3	72.5		7.7	76.1		5.8	81.7	
15	18.7	97.2		11.3	111.7		7.8	123.5	122.9	5.8	139.5	139.5
16	19.2	76.3	59.7	11.6	82.0		8.0	86.3		6.0	92.6	
17	19.4	92.2		11.8	104.3		8.1	114.2		6.0	127.9	
18	19.8	71.2		12.0	76.1		8.2	80.3		6.2	86.9	
19	19.5	89.2		11.8	100.2		8.1	109.3	109.3	6.1	121.8	
20	20.1	86.0	84.9	12.2	95.5	94.8	8.3	103.5		6.2	114.7	
21	20.3	81.8		12.3	89.9		8.4	96.8		6.3	106.7	
22	20.4	66.4	59.7	12.3	69.4	66.7	8.5	72.4		6.3	77.6	
23	20.6	76.9	74.8	12.5	83.3	84.5	8.6	88.9		6.4	97.4	
24	21.0	70.0	69.9	12.7	74.3	79.3	8.7	78.4	87.9	6.5	85.1	
25	21.1	82.9		12.8	89.0		8.7	93.6		6.5	100.4	
26	21.1	70.0	61.3	12.8	73.5	66.9	8.8	76.8	73.3	6.5	82.4	
27	21.1	78.8	80.6	12.8	84.7	87.7	8.8	89.6	95.7	6.5	97.0	106.4
28	21.2	63.5	59.7	12.8	65.3	66.1	8.8	67.5	73.6	6.5	71.8	
29	21.2	83.4	87.9	12.8	90.7	95.0	8.8	96.7	103.2	6.5	105.5	
30	21.4	81.0	91.1	12.9	87.0	96.4	8.9	91.8	103.8	6.6	98.9	112.7
31	21.6	72.9	69.1	13.1	76.6	76.6	8.9	79.9		6.7	85.5	
32	21.7	60.5		13.1	61.1	99.0	9.0	62.4		6.7	65.8	
33	21.8	74.2	96.6	13.2	78.2	104.3	9.0	81.7	112.5	6.7	87.6	

(see Table 3) occurring for a series of systems. Taking into account the chemical nature of the compounds studied, and also the value and the sign of $|\Delta U_S| - |\Delta U_{exp}|$ difference, one can distinguish two groups of solutions. The first group includes the systems that are formed by the solvents inclined to the specific IMIs. The calculation method suggested "works" for the solutions in which there is no noticeable change in the contribution from the specific interactions, compared to pure solvents. That is why the magnitude and sign of the $|\Delta U_S| - |\Delta U_{exp}|$ difference testifies to the strengthening ("minus") or weaking ("plus") of the energy of hydrogen

TABLE 2 (continued)

	IX. Acetone			X. Acetonitrile			XI. Dimethylformamide			XII. Dimethylsulphoxide		
No.	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$	$-\Delta U_{o-i}$	$-\Delta U_S$	$-\Delta U_{exp}$
1	5.9	60.1	52.7	10.0	60.0	52.4	2.2	73.1	66.6	10.6	80.8	81.6
2	6.2	56.5	48.4	10.5	56.9	49.8	9.4	72.3		11.1	76.3	
3	6.6	60.5		11.3	61.1		9.4	72.3	76.1	12.0	81.9	84.9
4	6.6	57.8	55.3	11.4	58.8	53.1	10.1	77.4	71.0	12.1	78.4	76.7
5	6.9	62.7	62.5	11.9	63.6		10.7	79.9		12.6	85.0	
6	6.7	69.5	70.4	11.5	69.5		10.3	88.7		12.2	93.6	
7	6.7	58.9	58.4	11.5	60.0	49.1	10.3	74.8		12.2	79.8	83.9
8	7.0	60.2		12.1	61.2		10.8	77.3		12.9	81.8	
9	8.0	62.4	57.4	14.0	64.2		12.6	80.7		15.1	85.6	
10	9.9	60.2		17.4	64.0	64.2	15.4	94.2	87.9	18.9	84.2	97.9
11	10.5	62.4	60.4	18.6	66.4	62.6	16.9	82.0		20.4	87.7	
12	11.1	60.5		19.8	65.4		18.0	79.4		21.8	85.7	
13	11.5	84.2	90.1	20.5	87.8		18.7	109.1		22.7	116.7	
14	11.9	59.5	58.4	20.9	65.1		19.1	78.3		23.2	85.0	
15	11.8	83.1		21.1	86.3		19.2	109.7		23.3	115.6	
16	12.2	67.4		21.7	72.9		19.8	88.1		24.0	95.5	
17	12.3	78.8	80.0	21.9	82.9	77.9	20.0	104.2	100.9	24.3	110.6	108.9
18	12.5	61.3		22.3	67.4		20.4	81.3		24.8	88.1	
19	12.4	76.3		22.0	80.7	73.8	20.1	101.0	95.6	24.5	107.4	105.2
20	12.7	73.5		22.6	78.3	68.1	20.8	97.5	92.8	25.2	104.1	101.9
21	12.8	69.9	63.2	22.9	75.4	66.9	21.0	92.9	89.3	25.6	99.6	99.9
22	12.9	56.9	56.4	23.0	63.7		21.1	75.8		25.6	82.7	81.5
23	13.0	65.4		23.3	71.5	62.3	21.4	87.2	85.0	26.0	94.0	94.3
24	13.3	59.3	60.8	23.7	66.1	59.9	21.4	87.2	86.4	26.5	86.2	92.4
25	13.3	73.0		23.8	79.2	80.4	21.9	95.7		26.6	104.0	
26	13.3	60.1		23.8	67.1	65.7	21.9	80.0		26.7	87.3	
27	13.3	68.0	73.4	23.9	74.4		21.9	90.0	90.4	26.7	97.7	98.9
28	13.4	54.1		23.9	61.6	61.4	21.9	72.5		26.8	79.6	
29	13.4	72.0		23.9	77.9		22.0	95.3		26.8	102.7	
30	13.5	70.6	81.5	24.1	76.9		22.2	93.1		27.0	110.1	109.4
31	13.6	62.9		24.4	70.0	70.6	22.2	93.1	85.3	27.4	91.2	94.8
32	13.7	51.2		24.5	59.3	72.3	22.5	69.1		27.5	76.2	
33	13.8	63.9		24.7	71.1		22.7	85.0		27.7	92.7	

bond between the molecules of solute and solvent, compared to the analogous characteristics between the molecules in the liquid. The magnitude of $|\Delta U_S| - |\Delta U_{exp}|$ for this group of systems is less than 10 kJ mol^{-1}.

The solutions in which one of the components is a polar solvent (A), and the other a non-polar solvent (B), refer to the second group. For the systems of (A/B) type, the difference $|\Delta U_S| - |\Delta U_{exp}|$ is positive; for (B/A) it is negative (in both cases less than 15 kJ mol^{-1}). We believe that the noted deviations of ΔU_S from ΔU_{exp} relate to the absence in the theoretical

TABLE 3

Deviations of the calculated from experimentally determined IMI energies (in kJ mol^{-1}) for the solutions of polar aromatic and aliphatic compounds in the solvents differing by the physicochemical properties at 298 K

No.	I[a]	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
1				6.4	13.6		20.3	16.6	7.4	7.6	6.5	−0.8
2	2.9	7.3		8.1					8.1	7.1		
3			−1.5								−3.8	−3.0
4	−2.5	2.0	3.2	3.0	16.3	14.6	12.1	5.7	2.5	5.7	6.4	1.7
5			0.8				11.3	4.9	0.2			
6									−0.9			
7			1.0	0.7	11.2		9.7	2.7	0.5	10.9		−4.1
8				2.4			−7.2	−13.4				
9				3.3				1.5	5.0			
10				0.0	11.4					−0.2	6.3	−13.7
11			−0.4	0.5	10.0		7.9	4.0	2.0	3.8		
12			−1.3									
13					−4.8				−5.9			
14				3.2					1.1			
15				−0.4			0.6					
16				4.4	16.6							
17	−7.1	−9.5		2.0					−1.2	5.0	3.3	1.7
18												
19										6.9	5.4	2.2
20					1.1	0.7				10.2	4.7	2.2
21									6.7	8.9	3.6	0.5
22			−2.2	−0.4	6.7	2.7			0.5			1.2
23				3.5	2.1	−1.2				9.2	2.2	−0.3
24	−18.5	12.1		−0.1	0.1	−5.0	−9.5		−1.5	6.2	0.8	−0.3
25										−1.2		
26				0.1	8.7	6.6	3.5			1.4		
27		−8.4			−1.8	−3.0	−6.1	−9.4	−5.4		−0.4	−1.2
28				−3.0	3.8	−0.8	−6.1			0.2		
29					−4.5		−6.5					
30		−7.8		−4.7	−10.0	−9.4	−11.4	−13.8	−10.9			0.7
31				−0.9	3.8	0.0				0.6	7.8	−3.6
32						−37.9				−13.0		
33					−22.4	−26.1	−30.8					

[a] Column headings are as given in Table 2.

method developed of the additional experimentally observed energetic expenditures upon solution formation, that relate to different capacities of the molecules of solute and solvent for solvophobic and solvophilic interactions [49, 50]. Indeed, in the solutions of (B/A) type, it is more energetically advantageous for the solvent molecules to interact between each other according to the solvophilic mechanism, but not according to the solvophobic mechansim with less polar solute molecules; hence, in order to form the solutions, it is necessary to preliminarily destroy the association bonds within the solvent (the difference sign is "minus"). In the systems of (A/B) type, the difference considered also reflects the presence of the solvophobic interaction. Here it comes to the aspiration of the dissolved solvophilic substances for self-association due to the absence of the forces for comparatively firm binding of the solvophilic particles with solvophobic solvent molecules (respectively, the sign of $|\Delta U_S| - |\Delta U_{exp}|$ difference is "plus").

Table 3 shows that the difference investigated is in some systems (e.g., solutions in formamide) somewhat higher than in others. One can suppose that IMIs in such systems are complicated by factors that are characteristic both of the first and of the second group of solutions.

CONCLUSIONS

The contributions from various constituents to the total solvation energy in the solutions of polar organic substances change essentially in the dependence on the electrooptic properties of solvents. In solutions formed by polar substances and non-polar solvents IMIs are mainly determined by the attractive forces occurring upon dispersion. In systems formed by polar compounds, the contribution from the orientation-induction IMIs, which is proportional to the dipole moment of the substance dissolved, assumes great importance. Here, the increase in ΔU_{o-i} values for the solutions considered is of non-linear character with the change in the dielectric properties of the solvents.

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