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Contributions of hydrocarbon radicals and functional groups of organic molecules to enthalpies of their solvation in mixed water—*tert*-butyl alcohol solvents

D. V. Batov[a]* *and V. P. Korolev*[b]

[a]*Institute of Chemistry of Non-Aqueous Solutions, Russian Academy of Sciences,*
1 ul. Akademicheskaya, 153045 Ivanovo, Russian Federation.
Fax: 007 (093 2) 37 8507
[b]*Ivanovo State Academy of Chemistry and Technology,*
7 prosp. F. Engel'sa, 153460 Ivanovo, Russian Federation.
Fax: 007 (093 2) 30 1826

The contributions of hydrocarbon radicals ($-CH_3$, $>CH_2$, $>CH-$, $>C<$) and functional groups ($-OH$, $-OCOO-$, $-NO_2$, $-CN$, $>SO$) to the enthalpies of solvation of organic molecules in mixed water—*tert*-butyl alcohol solvents were calculated in the whole range of compositions at 298.15 K. The influence of the composition and properties of the mixture on the solvation of different functional groups is discussed.

Key words: enthalpy of solvation, hydrocarbon radical, functional group, mixed solvents, water, *tert*-butyl alcohol.

Data on group contributions to energy parameters of solvation are known[1—4] only for water and several nonaqueous solvents, while this information is almost absent for mixed solvents. At the same time, the problem of additivity of properties of organic compounds, including their properties in solutions, is rather urgent, because only studies of simple objects give information on more complex organic molecules. This work continues systematic studies of the solvation of organic molecules[5—8] in water-alcohol mixtures and is devoted to the determination of the contributions of the hydrocarbon radicals and polar groups of molecules in $H_2O—Bu^tOH$ mixtures.

The enthalpy of solvation ($\Delta_s H°$) of a nonelectrolyte molecule consisting of the hydrocarbon R radical and n functional Y groups can be expressed through the group contributions as follows:

$$\Delta_s H°(RY_n) = a_0 + \Delta_s H°(R) + \sum^{j} n_j \Delta_s H°(Y_j), \tag{1}$$

where a_0 is the coefficient in Eq. (2) for n-alkanes,

$$\Delta_s H° = a_0 + a_1 V_w, \tag{2}$$

where V_w is the van der Waals molar volume of alkane.

The determination of group contributions in the enthalpy of solvation of organic molecules in $H_2O—Bu^tOH$ mixtures in the whole range of compositions was difficult, since experimental data on enthalpies of solvation of hydrocarbons, which are necessary for determining the contributions of the corresponding radicals to the enthalpy of solvation, were not available. We obtained these data in another study. Using the regularities established, we calculated the coefficients in Eq. (2), which are presented in Table 1. The contribution of the hydrocarbon radicals to the enthalpy of solvation determined from Eqs. (3a)—(3d) is presented in Fig. 1.

Table 1. Coefficients of Eq. (2) for enthalpies of solvation of alkanes in the mixed $H_2O—Bu^tOH$ solvent at 298.15 K

X_{Bu^tOH}	a_0	$-a_1$	X_{Bu^tOH}	a_0	$-a_1$
0.00	−12.81	0.272	0.30	1.75	0.426
0.05	−1.68	0.324	0.50	1.00	0.435
0.10	1.60	0.364	0.75	0.95	0.429
0.20	2.34	0.408	0.90	1.11	0.424
			1.00	1.25	0.421

$$\Delta_s H°(-CH_3) = 13.67 \cdot a_1, \tag{3a}$$

$$\Delta_s H°(>CH_2) = 10.23 \cdot a_1, \tag{3b}$$

$$\Delta_s H°(>CH-) = 6.78 \cdot a_1 + 1.3, \tag{3c}$$

$$\Delta_s H°(>C<) = 3.33 \cdot a_1 + 4.6. \tag{3d}$$

The coefficients in Eqs. (3a)—(3d) are numerically equal to the van der Waals molar volumes of the corresponding hydrocarbon radicals taken from Ref. 9. The increase in the enthalpies of solvation of the >CH— and >C< radicals by 1.3 and 4.6 kJ mol^{-1}, respectively, is related to the fact that the enthalpies of evaporation of hydrocarbons containing the tertiary and quaternary C

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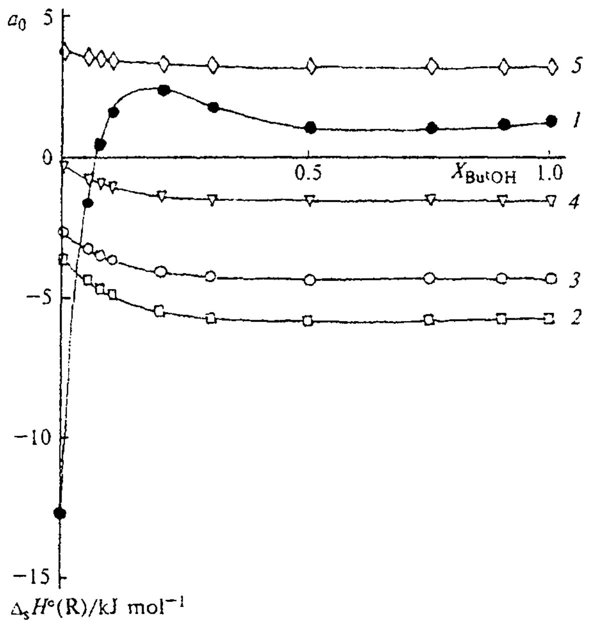

Fig. 1. Dependences of enthalpies of solvation ($\Delta_s H^\circ$) of hydrocarbon radicals in the $H_2O—Bu^tOH$ mixture and of the a_0 coefficient in Eq. (2) (curve *1*) on the composition of the solvent (*X*) at 298.15 K: $—CH_3$ (*2*), $>CH_2$ (*3*), $>CH—$ (*4*), and $>C<$ (*5*).

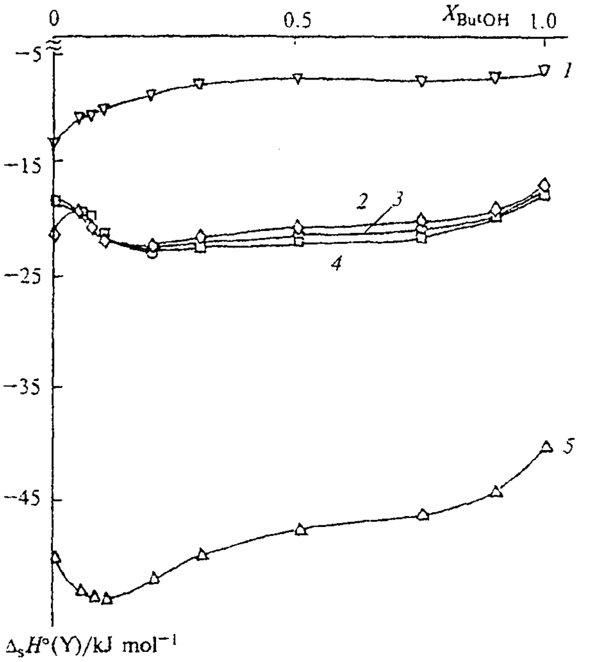

Fig. 2. Dependences of enthalpies of solvation ($\Delta_s H^\circ$) of functional groups in the mixed $H_2O—Bu^tOH$ solvent on its composition (*X*) at 298.15 K: —O— (*1*), —OCOO— (*2*), —CN (*3*), $—NO_2$ (*4*), and >SO (*5*).

atoms are 1.3 and 4.6 kJ mol^{-1} lower, respectively, than the corresponding enthalpies of evaporation of *n*-alkanes.[10] Enthalpies of dissolution are independent of the alkane structure.[10,11]

The a_0 coefficient in Eq. (2) corresponds to the enthalpy of solvation of alkane when $V_w = 0$. This value is determined only by the solvent nature. The change in the a_0 coefficient at different compositions of the mixture has an extreme character with a maximum in the range of concentrations of Bu^{t}OH equal to 0.2 molar fractions (m.f.) and an insignificant minimum in the range of 0.6 m.f. Bu^{t}OH. The change in solvation of the a_0 contribution determines mainly the character of nonspecific solvation of compounds in the mixed solvent studied.

The data presented in Fig. 1 show that the solvation of the $—CH_3$, CH_2, $>CH—$, and $>C<$ radicals increases insignificantly as the content of the alcohol in the mixed solvent increases to 0.2 m.f. Bu^{t}OH. In the composition range of 0.2—1.0 m.f. Bu^{t}OH, the enthalpies of solvation of these groups remain almost unchanged. The aforesaid can be evidence that the properties of the mixed solvent, which determine nonspecific solvation, are constant.

Using Eq. (3), we calculated the increments of the functional groups (Y = $—NO_2$, —CN, —OCOO—, >SO, —O—, —OH) (Fig. 2) to the enthalpies of solvation of molecules of acetonitrile (**1**), nitromethane (**2**), propylene carbonate (**3**), dimethylsulfoxide (**4**), 2-ethoxyethanol (**5**), *tert*-butyl alcohol (**6**), ethylene glycol (**7**), 2,3-butylene glycol (**8**), 1,4-butylene glycol (**9**), and glycerol (**10**) in the $H_2O—Bu^tOH$ mixture:

$$\Delta_s H^\circ(—CN) = \Delta_s H^\circ(\mathbf{1}) - a_0 - \Delta_s H^\circ(—CH_3), \quad (4)$$

$$\Delta_s H^\circ(—NO_2) = \Delta_s H^\circ(\mathbf{2}) - a_0 - \Delta_s H^\circ(—CH_3), \quad (5)$$

$$\Delta_s H^\circ(—OCOO—) = \Delta_s H^\circ(\mathbf{3}) - a_0 - \Delta_s H^\circ(—CH_3) - \Delta_s H^\circ(CH_2) - \Delta_s H^\circ(>CH—), \quad (6)$$

$$\Delta_s H^\circ(>SO) = \Delta_s H^\circ(\mathbf{4}) - a_0 - 2\cdot\Delta_s H^\circ(—CH_3), \quad (7)$$

$$\Delta_s H^\circ(—O—) = \Delta_s H^\circ(\mathbf{5}) - a_0 - \Delta_s H^\circ(—CH_3) - 3\cdot\Delta_s H^\circ(>CH_2) - \Delta_s H^\circ(—OH), \quad (8)$$

$$\Delta_s H^\circ(—OH) = \Delta_s H^\circ(\mathbf{6}) - a_0 - 3\cdot\Delta_s H^\circ(—CH_3) - \Delta_s H^\circ(>C<), \quad (9)$$

$$\Delta_s H^\circ(—OH) = [\Delta_s H^\circ(\mathbf{7}) - a_0 - 2\cdot\Delta_s H^\circ(—CH_2)]/2, \quad (10)$$

$$\Delta_s H^\circ(—OH) = [\Delta_s H^\circ(\mathbf{8}) - a_0 - 2\cdot\Delta_s H^\circ(—CH_3) - 2\cdot\Delta_s H^\circ(>CH—)]/2, \quad (11)$$

$$\Delta_s H^\circ(—OH) = [\Delta_s H^\circ(\mathbf{9}) - a_0 - 4\cdot\Delta_s H^\circ(—CH_2)]/2, \quad (12)$$

$$\Delta_s H^\circ(—OH) = [\Delta_s H^\circ(\mathbf{10}) - a_0 - 2\cdot\Delta_s H^\circ(>CH_2) - \Delta_s H^\circ(>CH—)]/3. \quad (13)$$

The enthalpies of solvation of the compounds are presented in Table 2.

Table 2. Enthalpies of solvation ($-\Delta_s H^\circ$) of compounds **1—10** in the mixed H_2O—Bu^tOH solvent at 298.15 K

$X_{\mathrm{Bu^tOH}}$	$-\Delta_s H^\circ$/kJ mol^{-1}									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
0.000	34.5	34.9	41.0	70.5	65.5	64.0	68.1	73.9	86.6	91.4
0.050	25.5	25.6	29.8	64.2	54.4	51.7	63.1	64.6	79.9	86.6
0.075	25.0	24.1	29.7	63.1	52.9	48.2	62.5	63.1	79.6	86.0
0.100	25.2	24.9	30.3	62.7	51.5	46.5	62.5	61.7	79.3	86.0
0.200	26.1	25.9	31.5	61.3	50.2	45.9	62.5	60.4	79.0	86.3
0.300	26.2	26.6	31.8	60.2	49.5	46.0	62.5	59.7	78.8	86.5
0.500	26.4	27.1	31.8	58.8	49.3	45.9	62.9	59.2	79.2	87.0
0.750	26.0	26.7	31.2	57.3	49.5	46.6	63.1	59.3	80.3	87.2
0.900	24.7	24.3	29.8	54.9	48.7	47.1	63.0	58.6	81.0	86.0
1.000	22.1	22.4	27.4	50.7	47.2	46.8	62.3	57.0	81.4	84.0
$\Delta_{\mathrm{vap}}H$	33.2	38.3	42.8	52.9	47.2	46.8	61.1	76.5	59.0	85.8

Note. The enthalpies of solvation of the compounds were calculated using the formula $\Delta_s H^\circ = \Delta_{\mathrm{sol}}H^\circ - \Delta_{\mathrm{vap}}H$. The enthalpies of dissolution ($\Delta_{\mathrm{sol}}H$) were calculated from the data in Refs. 7, 8, and 12; and the enthalpies of evaporation ($\Delta_{\mathrm{vap}}H$) were calculated using the data in Ref. 13.

The enthalpy of solvation of *tert*-butyl alcohol was determined as the difference between the relative partial molar enthalpy (see Eq. (13)) and the enthalpy of evaporation ($\bar{h}^\circ$).

$$\bar{h}^\circ_{\mathrm{Bu^tOH}} = H^E + (1 - X_{\mathrm{Bu^tOH}})\cdot(\partial H^E/\partial X_{\mathrm{Bu^tOH}}) \tag{14}$$

The enthalpy of mixing water with *tert*-butyl alcohol (H^E/kJ mol^{-1})[15] is described by the ninth-power polynomial relative to $X_{\mathrm{Bu^tOH}}$, whose coefficients are the following: $a_0 = 0.02$, $a_1 = -22.68$, $a_2 = 285.42$, $a_3 = -1759.6$, $a_4 = 6384.8$, $a_5 = -14348$, $a_6 = 20219$, $a_7 = -17395$, $a_8 = 8345.7$, $a_9 = 1710.0$. In calculating the enthalpy of hydration of Bu^{t}OH, the value of the standard enthalpy of dissolution (−17.2 kJ mol^{-1})[1] was used, which was obtained from the calorimetric data in the region of small concentrations of the dissolved compound.

For determining the enthalpy of solvation of the hydroxy group in Eq. (8), $\Delta_s H^\circ$(—OH) of 2,3-butylene glycol was used. 2,3-Butylene glycol is an isomer of 2-ethoxyethane; its molecule polar groups are located at adjacent C atoms.

In the whole range of compositions of the mixture, the solvation of the functional groups increases in the series O < OCOO ≤ CN ≤ NO_2 < OH(**8**) < OH(**10**) < OH(**7**) < OH(**9**) < OH(**6**) < SO. Differences from this series are observed only for $\Delta_s H^\circ$ of the functional groups of acetonitrile, nitromethane, and propylene carbonate for which (—OCOO—) < (—NO_2) < (—CN).

The enthalpies of solvation of the —CN, —NO_2, and —OCOO— groups are very close in the whole range of compositions of the mixed solvent. This can be related to insignificant differences in their electron-acceptor and electron-donor (except nitromethane) properties and in sizes (Table 3). The enthalpies of solvation of these groups remain almost unchanged within the composition range of 0.2—1.0 m.f. Bu^{t}OH. This can be evidence for an insignificant change in electron-donor properties as the composition of the mixed solvent is varied. This conclusion can be also confirmed by the close values of donor numbers of the components of the mixture: water and *tert*-butyl alcohol (see Table 3).

The sulfo and hydroxy groups with predominantly electron-donor properties are characterized by the more pronounced dependences of the enthalpies of solvation on the composition of the mixture. In the composition range of 0.1—1.0 m.f. Bu^{t}OH, the solvation of the >SO and —O— groups weakens noticeably. This is explained by a decrease in the electron-acceptor ability of molecules of the medium (Fig. 3). The E_T values of the mixture were determined from Eq. (11) obtained[17] for

Table 3. Van der Waals molar volumes (V_w) and donor-acceptor properties (DN, E_T) of dissolved compounds and solvents at 298.15 K

Compound	V_w(R)	V_w(Y)	DN	E_T
Acetonitrile	13.67	14.70	14.1	46.0
Nitromethane	13.67	16.80	2.7	46.2
Propylene carbonate	30.68	19.1	15.1	46.6
Dimethylsulfoxide	27.34	17.37	29.8	45.1
2-Ethoxyethanol	44.36	5.2[a]	—	50.8
tert-Butyl alcohol	44.34	8.04	38	43.9
Ethylene glycol	20.46	8.04[b]	20[c]	56.3[c]
1,4-Butylene glycol	40.92	8.04[b]	—	—
2,3-Butylene glycol	40.90	8.04[b]	—	—
Glycerol	27.24	8.04[b]	19	57.0
Water	—	—	33.2	63.1

Note. The values of V_w/cm^3 mol^{-1} were obtained from Ref. 9; DN/kcal mol^{-1}, Ref. 15; E_T, Ref. 16.

[a] V_w for the —O— group. [b] The V_w value is presented for one OH group. [c] Values for ethylene glycol.

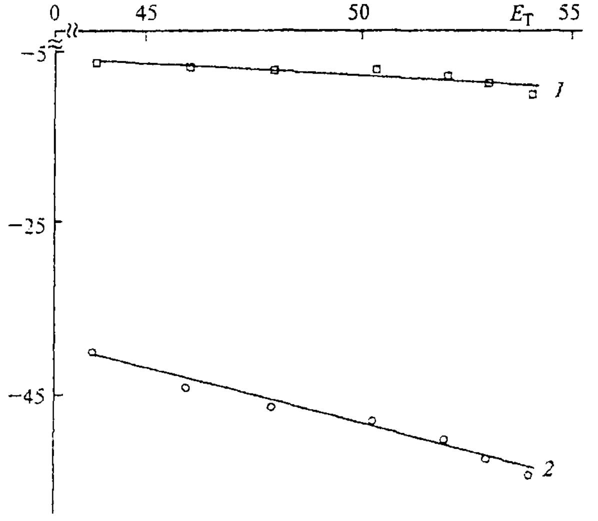

Fig. 3. Dependences of enthalpies of solvation ($\Delta_sH°$) of hydroxy (*1*) and sulfo groups (*2*) in the mixed H_2O—Bu^{t}OH solvent on the electron-acceptor ability of the mixture (E_T) at 298.15 K.

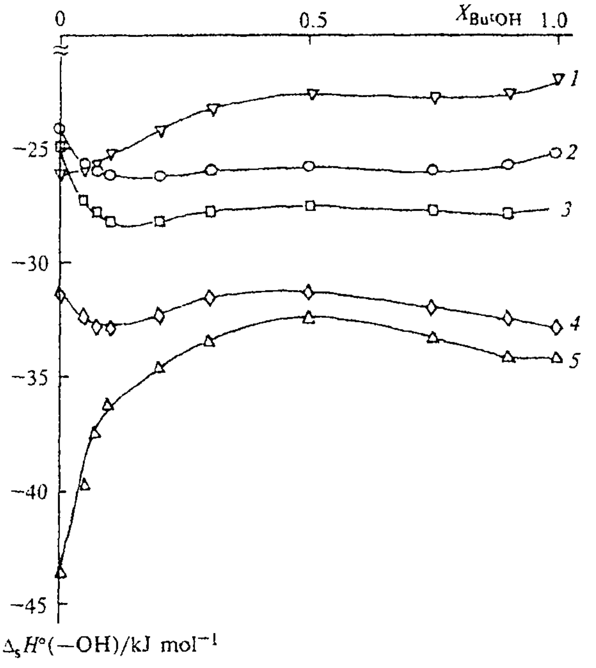

Fig. 4. Dependences of enthalpies of solvation ($\Delta_sH°$) of hydroxyl groups of 2,3-butylene glycol (*1*), glycerol (*2*), ethylene glycol (*3*), 1,4-butylene glycol (*4*), and *tert*-butyl alcohol (*5*) in the mixed H_2O—Bu^{t}OH solvent on its composition at 298.15 K.

the composition range of 0.06—33.2 mole H_2O per liter or 0.1—0.99 m.f. Bu^{t}OH.

$$E_T = 43.9 + 2.82 \cdot \ln(C_{H_2O}/1.01 + 1), \qquad (15)$$

where C_{H_2O} is the molar concentration of water in the mixture.

The enthalpies of solvation of the hydroxy groups of *tert*-butyl alcohol, ethylene glycol, 1,4- and 2,3-butylene glycols, and glycerol are presented in Fig. 4. In the whole range of compositions of the mixture, the enthalpies of solvation of the monofunctional Bu^{t}OH are the most exothermic, because the mutual effect of functional groups of the same nature are absent. The solvation of the hydroxyl groups decreases as the number of OH groups in the alcohol molecule increases, *i.e.*, in the *tert*-butyl alcohol—ethylene glycol—glycerol series. The mutual effect of hydroxyl groups decreases when they diverge. This may explain the fact that the $\Delta_sH°(-OH)$ values for 1,4-butylene glycol are more negative than those for ethylene glycol. The enthalpy of solvation of the OH group of 2,3-butylene glycol is more endothermic that $\Delta_sH°$ of OH groups of diols and glycerol. We observed the similar decrease in the solvation of the hydroxyl group of 2,3-butylene glycol in the case of the water-methanol solvent[18] and explained this by the formation of the intramolecular bond in 2,3-butylene glycol.

A change in the composition of the mixed solvent affects insignificantly the enthalpies of solvation of hydroxyl groups in the range of $X_{Bu^tOH} > 0.2$ m.f. The strongest change in $\Delta_sH°(-OH)$ occurs when additions of *tert*-butyl alcohol are small ($X_{Bu^tOH} < 0.2$ m.f.). An increase in the content of Bu^{t}OH in the mixture results in a decrease in solvation of the OH group of polyhydric alcohol and its enhancement in the case of di- and trihydric alcohols.

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References

1. V. P. Belousov and M. Yu. Panov, *Termodinamika vodnykh rastvorov neelektrolitov* [*Thermodynamics of Aqueous Solutions of Nonelectrolytes*], Khimiya, Leningrad, 1983, 264 pp. (in Russian).
2. S. Cabani and P. Gianni, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1184.
3. R. Fuchs and W. K. Stephenson, *Can. J. Chem.*, 1985, **63**, 349.
4. V. I. Smirnov and G. A. Krestov, *Zh. Khim. Termodin. Termokhim.* [*J. Chem. Thermodyn. Thermochem.*], 1993, **2**, 5 (in Russian).
5. O. A. Antonova, D. V. Batov, and V. P. Korolev, *Zh. Obshch. Khim.*, 1993, **63**, 2200 [*J. Gen. Chem.*, 1993, **63** (Engl. Transl.)].
6. O. A. Antonova, D. V. Batov, and V. P. Korolev, *Zh. Obshch. Khim.*, 1994, **64**, 1253 [*J. Gen. Chem.*, 1994, **64** (Engl. Transl.)].
7. D. V. Batov, N. G. Egorova, A. F. Svishchev, and V. P. Korolev, *Zh. Obshch. Khim.*, 1994, **64**, 1761 [*J. Gen. Chem.*, 1994, **64** (Engl. Transl.)].
8. D. V. Batov, O. A. Antonova, N. G. Egorova, and V. P. Korolev, *Zh. Obshch. Khim.*, 1996, in press [*J. Gen. Chem.*, 1996, in press (Engl. Transl.)].
9. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

10. B. N. Solomonov and A. I. Konovalov, *Usp. Khim.*, 1991, **60**, 45 [*Russ. Chem. Rev.*, 1991, **60** (Engl. Transl.)].
11. D. V. Batov and V. P. Korolev, *Zh. Obshch. Khim.*, 1992, **62**, 2429 [*J. Gen. Chem.*, 1992, **62** (Engl. Transl.)].
12. N. G. Manin, O. A. Antonova, and V. P. Korolev, *Zh. Obshch. Khim.*, 1996, **66**, 1271 [*J. Gen. Chem.*, 1996, **66** (Engl. Transl.)].
13. Y. Marcus, *Ion Solvation*, Wiley, New York, 1985, 306 pp.
14. V. P. Belousov and A. G. Morachevskii, *Teploty smesheniya zhidkostei* [*Heats of Mixing of Liquids*], Khimiya, Leningrad, 1970, 256 pp. (in Russian).
15. Y. Marcus, *J. Solut. Chem.*, 1984, **13**, 599.
16. Ch. Reichard, *Solvent Effects in Organic Chemisrty*, Verlag Chemie, Berlin, 1979.
17. H. Langhals, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 724.
18. D. V. Batov, O. A. Antonova, N. G. Egorova, and V. P. Korolev, *Zh. Obshch. Khim.*, 1996, **66**, 214 [*J. Gen. Chem.*, 1996, **66** (Engl. Transl.)].

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