Enthalpies of dissolution of propylene carbonate, acetonitrile, and 1,4-dioxane in mixtures of water with acetone or dimethyl sulfoxide

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Enthalpies of dissolution of acetonitrile, propylene carbonate, and 1,4-dioxane in mixtures of water with acetone or DMSO were measured in the whole concentration range of the mixed solvents. Standard enthalpies of dissolution and enthalpies of transfer of solutes from water to its mixtures with acetone or DMSO were determined. In the region of small proportions of the nonaqueous component, the enthalpy of cavity formation in the mixed solvent makes the main contribution to the variation of the enthalpy of dissolution. An increase in the proportion of the nonaqueous component leads to competition between the contributions of cavity formation and specific interaction between the solute and the solvent during solvation.

Key words: enthalpy of dissolution, enthalpy of transfer, enthalpy of cavity formation; nonelectrolytes; mixed solvents.

Study of aqueous-organic mixed solvents is of both scientific and practical interest. Despite the fact that these solvents are widely used in technology, their solvating abilities, structural properties, and the nature of intermolecular interactions have not been adequately studied. The question of what effects the electrolytes added exert on the structures of both the components of the mixture and the mixed aqueous-organic solvents is also significant. In this connection, it has been of interest to elucidate how the substance added affects intermolecular interactions, solvation, and associative equilibria in a solution and to study their variation with the concentrations of the components of the system. The published data do not allow one to unambiguously answer the foregoing questions. This is due most of all to the fact that no systematic approach to the investigation of solutions has been used.

Previously[1,2] data on the enthalpies of dissolution of a large number of various compounds in a water—DMF mixture were obtained for the whole range of compositions of the mixed solvent. However, the primary attention has been concentrated on distinguishing hydrophobic and hydrophilic effects, *i.e.*, various forms of the effect of the solute on strengthening or destruction of the structure of water, caused by the hydrophobic or hydrophilic character of hydration.[3] Therefore, only the so-called "water-like region," *i.e.*, the region of low concentrations of the nonaqueous component, has been considered. However, the regions of compositions in which hydrophobic effects compete with other kinds of intermolecular interactions also present considerable interest. Among these, specific interactions of electron-donating and electron-withdrawing atoms of the solute with the solvent, caused by donor-acceptor properties of both the solute and the aqueous-organic mixed solvent, are of great importance. The addition of a component with pronounced donor or acceptor properties to water determines to a large extent the solvating ability of the mixed solvent over the whole range of its compositions.[4] Therefore, the enthalpy characteristics of nonelectrolytes in aqueous-organic solutions are very complicated to interpret. This is probably the reason why Cox, who obtained very interesting data concerning the heats of dissolution of a great number of nonelectrolytes in H_2O—DMSO mixtures[5] (as well as most of the other researchers), restricted himself to illustration of only the dependences obtained (see Ref. 5).

Experimental

The integral heats of dissolution of acetonotrile (AN), propylene carbonate (PC), and 1,4-dioxane (DO) in mixtures of water with acetone (Me_2CO) or DMSO were measured on a precision isoperibolic calorimeter with an error of 0.5 %. The studies were carried out over the whole range of compositions of the aqueous-organic mixed solvents at 298.15 K. The compounds used in the study were purified by known procedures.[6,7]

Results and Discussion

The values of the enthalpies of dissolution obtained ($\Delta_{ds}H^m$) are listed in Table 1. Assuming that in the given region of compositions the $\Delta_{ds}H^m$ values do not depend

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Table 1. Enthalpies of dissolution ($\Delta_{ds}H^m$/kJ mol^{-1}) of acetonitrile, dioxane, and propylene carbonate in water—nonelectrolyte mixtures (Me_2CO, DMSO) at 298.15 K

Acetonitrile		Dioxane		Propylene carbonate	
m*	$\Delta_{ds}H^m$	m	$\Delta_{ds}H^m$	m	$\Delta_{ds}H^m$
		Water—acetone			
X_{Me_2CO} = 0.0**		X_{Me_2CO} = 0.0		X_{Me_2CO} = 0.0	
0.0450	−1.56	0.0297	−9.63	0.0340	1.36
0.0711	−1.41	0.0338	−9.61	0.0346	1.35
0.0808	−1.44	0.0612	−9.49	0.0612	1.73
0.0813	−1.41	0.0933	−9.37	0.0847	1.48
0.0998	−1.41	0.1175	−9.34	0.1003	1.65
$\Delta_{ds}H^\circ$ = −1.44±0.12		$\Delta_{ds}H^\circ$ = −9.49±0.15		$\Delta_{ds}H^\circ$ = 1.52±0.20	
X_{Me_2CO} = 0.06		X_{Me_2CO} = 0.06		X_{Me_2CO} = 0.06	
0.0392	2.82	0.0297	−3.25	0.0397	6.68
0.0951	2.94	0.0490	−3.21	0.0983	6.79
0.1633	3.04	$\Delta_{ds}H^\circ$ = −3.23±0.02		0.1555	6.67
$\Delta_{ds}H^\circ$ = 2.93±0.10				$\Delta_{ds}H^\circ$ =6.77±0.10	
X_{Me_2CO} = 0.10		X_{Me_2CO} = 0.13		X_{Me_2CO} = 0.12	
0.0415	4.34	0.0259	−0.81	0.0460	8.28
0.0818	4.43	0.0568	−0.83	0.1255	8.31
0.1503	4.52	$\Delta_{ds}H^\circ$ = −0.82±0.01		0.1985	8.27
$\Delta_{ds}H^\circ$ = 4.43±0.09				$\Delta_{ds}H^\circ$ = 8.29±0.02	
X_{Me_2CO} = 0.18		X_{Me_2CO} = 0.31		X_{Me_2CO} = 0.19	
0.0500	4.65	0.0207	1.06	0.0424	7.80
0.1108	4.70	0.0595	1.03	0.0643	7.73
0.1917	4.85	$\Delta_{ds}H^\circ$ = 1.05±0.02		0.1564	7.66
$\Delta_{ds}H^\circ$ = 4.73±0.10				$\Delta_{ds}H^\circ$ =7.74±0.12	
X_{Me_2CO} = 0.30		X_{Me_2CO} = 0.52		X_{Me_2CO} = 0.52	
0.0613	4.10	0.0311	1.04	0.0521	3.37
0.1231	4.13	0.0552	1.12	0.0731	3.35
0.2192	4.07	$\Delta_{ds}H^\circ$ = 1.08±0.04		0.1209	3.36
$\Delta_{ds}H^\circ$ = 4.10±0.03				$\Delta_{ds}H^\circ$ = 3.36±0.01	
X_{Me_2CO} = 0.43		X_{Me_2CO} = 0.76		X_{Me_2CO} = 0.75	
0.0633	2.76	0.0432	1.06	0.0468	1.33
0.1369	2.74	0.0934	1.10	0.1221	1.29
0.2076	2.72	$\Delta_{ds}H^\circ$ = 1.08±0.02		0.1569	1.25
$\Delta_{ds}H^\circ$ = 2.74±0.02				$\Delta_{ds}H^\circ$ = 1.29±0.04	
X_{Me_2CO} = 0.68		X_{Me_2CO} = 0.91		X_{Me_2CO} = 0.91	
0.0321	1.11	0.0546	0.68	0.0564	0.52
0.0935	1.02	0.1074	0.65	0.1301	0.49
0.1642	1.01	$\Delta_{ds}H^\circ$ = 0.67±0.02		0.1889	0.45
$\Delta_{ds}H^\circ$ = 1.05±0.05				$\Delta_{ds}H^\circ$ = 0.49±0.04	
X_{Me_2CO} = 0.91		X_{Me_2CO} = 1.00		X_{Me_2CO} = 1.00	
0.0502	−0.14	0.0272	0.61	0.0324	0.23
0.1324	−0.17	0.0524	0.58	0.0938	0.24
0.1998	−0.17	$\Delta_{ds}H^\circ$ = 0.60±0.02		0.1639	0.23
$\Delta_{ds}H^\circ$ = −0.16±0.02				$\Delta_{ds}H^\circ$ = 0.24±0.01	
X_{Me_2CO} = 1.00					
0.0456	−0.53				
0.0954	−0.54				
0.1547	−0.55				
$\Delta_{ds}H^\circ$ = −0.54±0.01					
		Water—DMSO			
X_{DMSO} = 0.06		X_{DMSO} = 0.02		X_{DMSO} = 0.02	
0.1212	1.70	0.9338	−7.32	0.0789	3.02
0.1624	1.72	0.1031	−7.53	0.0810	3.14
$\Delta_{ds}H^\circ$ = 1.71±0.01		$\Delta_{ds}H^\circ$ = −7.42±0.11		0.2099	3.08
				$\Delta_{ds}H^\circ$ = 3.08±0.06	

Table 1 (continued)

Acetonitrile		Dioxane		Propylene carbonate	
m*	$\Delta_{ds}H^m$	m*	$\Delta_{ds}H^m$	m	$\Delta_{ds}H^m$
X_{DMSO} = 0.11		X_{DMSO} = 0.05		X_{DMSO} = 0.20	
0.1413	4.01	0.0765	−5.22	0.1465	8.27
0.2021	4.02	0.0779	−5.22	0.2048	8.36
$\Delta_{ds}H^\circ$= 4.02±0.01		$\Delta_{ds}H^\circ$ = −5.22±0.00		0.2769	8.26
				$\Delta_{ds}H^\circ$ = 8.30±0.06	
X_{DMSO} = 0.22		X_{DMSO} = 0.12		X_{DMSO} = 0.28	
0.1279	5.92	0.0754	−1.44	0.0798	8.72
0.2021	5.97	0.0963	−1.64	0.1165	8.61
$\Delta_{ds}H^\circ$ = 5.94±0.03		$\Delta_{ds}H$ = −1.54±0.10		0.1937	8.72
				$\Delta_{ds}H^\circ$ = 8.68±0.07	
X_{DMSO} = 0.33		X_{DMSO} = 0.20		X_{DMSO} = 0.38	
0.1042	5.09	0.0908	2.20	0.0958	6.89
0.1585	5.18	0.1168	2.03	0.1631	6.69
$\Delta_{ds}H^\circ$ = 5.14±0.05		$\Delta_{ds}H^\circ$ = 2.11±0.09		0.1910	6.93
				$\Delta_{ds}H^\circ$ = 6.84±0.15	
X_{DMSO} = 0.56		X_{DMSO} = 0.28		X_{DMSO} = 0.48	
0.0789	2.67	0.0488	4.05	0.0867	5.53
0.1436	2.73	0.1023	4.71	0.1836	5.47
$\Delta_{ds}H^\circ$ = 2.70±0.03		$\Delta_{ds}H^\circ$ = 4.38±0.33		$\Delta_{ds}H^\circ$ = 5.50±0.03	
X_{DMSO} = 0.72		X_{DMSO} = 0.38		X_{DMSO} = 0.68	
0.0624	1.43	0.0818	4.9	0.0971	3.19
0.1143	1.47	0.1566	4.7	0.1118	3.33
$\Delta_{ds}H^\circ$ = 1.45±0.02		$\Delta_{ds}H^\circ$ = 4.88±0.1		0.2321	3.02
				$\Delta_{ds}H^\circ$ = 3.18±0.15	
X_{DMSO} = 0.89		X_{DMSO} = 0.48		X_{DMSO} = 0.82	
0.0716	0.49	0.0622	4.15	0.0876	2.36
0.1348	0.51	0.0710	3.90	0.2116	2.39
$\Delta_{ds}H^\circ$ = 0.50±0.01		0.1143	4.30	$\Delta_{ds}H^\circ$ = 2.37±0.02	
		$\Delta_{ds}H^\circ$ = 4.12±0.05			
X_{DMSO} = 1.00		X_{DMSO} = 0.82		X_{DMSO} = 1.00	
0.0683	0.06	0.0658	2.03	0.1113	1.41
0.1263	0.07	0.1450	2.14	0.1237	1.42
$\Delta_{ds}H^\circ$ = 0.07±0.02		$\Delta_{ds}H^\circ$ = 2.09±0.05		0.1833	1.46
				$\Delta_{ds}H^\circ$ = 1.43±0.03	
		X_{DMSO} = 1.00			
		0.0592	1.81		
		0.0617	1.81		
		0.0855	1.62		
		0.0935	1.58		
		0.0953	1.63		
		0.1059	1.73		
		$\Delta_{ds}H^\circ$ = 1.70±0.12			

* Here m/mol kg^{-1} is the molality of a solute. ** X is the mole fraction of the nonaqueous component.

on the composition of the mixed solvent within the limits of experimental error, we took their average values, $(\Delta_{ds}H^m)_{av}$, as being equal to the standard enthalpies of dissolution $\Delta_{ds}H^\circ$.

The choice of the subjects of investigation was determined by the fact that PC and AN have practically identical donor and acceptor numbers, and the acceptor number of DO is approximately twice as high as these. However, the van der Waals molar volume (V_w) of PC is almost twice as high as V_w of AN, but is virtually equal to V_w of DO. DMSO and acetone are aprotic solvents that differ in their donor-acceptor properties. Some characteristics of the compounds studied are given in Table 2.

Table 2. Some characteristics of the compounds used in the study

Compound	DN_{SbCl_5}[a]	AN_{Et_3PO}[b]	V_{mol}	V_w[c]
PC	15.1	18.3	85.09	52.78
AN	14.1	18.9	52.84	28.37
1,4-DO	14.8	10.8	85.70	51.32
H_2O	18.0	54.8	18.07	12.08
DMSO	29.8	19.3	71.32	44.71
Me_2CO	17.0	12.5	74.04	39.04
MeOH	18.9	33.0	40.74	20.67
EtOAc	17.1	9.3	98.50	52.97
Bu^{t}OAc	13.4	—	132.58	73.43

[a] Published data.[14] [b] Published data.[12] [c] Published data.[15]

The effects of the addition of various compounds on intermolecular interactions in a solution are manifested in the character of $\Delta_{ds}H° = f(X_S)$ dependences, where X_S is the mole fraction of the nonaqueous component in the mixed solvent. Analysis of the donor-acceptor nature of the solute—solvent and solvent—solvent interactions, resorting to the published data on the thermochemistry of dissolution of nonelectrolytes in mixed solvents, made it possible to distinguish three types of dependences.[4] The $\Delta_{ds}H° = f(X_S)$ dependences, in which with increase in the concentration of the nonaqueous component in the mixed solvent, the endo contribution to the $\Delta_{ds}H°$ value predominates, belong to the first type. This type of dependences is typical of dissolution of an electron-donating substance in a mixture of water with an H-donor (for example, for solutions of hexamethylphosphotriamide or DO in aqueous alcohols). The $\Delta_{ds}H° = f(X_S)$ dependences with a clear-cut endo maximum belong to the second type. These are characteristic of a wide range of systems, in particular, solutions of electron-donating substances in mixtures of water with nonelectrolytes of various donor-acceptor natures, for example, solutions in mixtures of water with electron-donating nonelectrolytes. The dependences in which exo contribution to the $\Delta_{ds}H°$ value predominates belong to the third type. These dependences are found much more rarely and are characteristic of solutions of electron-withdrawing substances in mixtures of water with some electron-withdrawing nonelectrolytes (H-donors). Solutions of PC or nitromethane in water—carbamide mixtures and solutions of carbamide in H_2O—PC mixtures fit into this group.[4]

Figure 1 presents curves for standard enthalpies of transfer ($\Delta_{tr}H°$) of DO from water to H_2O—S mixtures (S is DMSO, Me_2CO, or MeOH). The data for solutions of DO in H_2O—MeOH mixtures were taken from the literature.[8] Analogous dependences[5] for solutions of ethyl acetate (EtOAc) and *tert*-butyl acetate (Bu^{t}OAc) in H_2O—DMSO mixtures are also presented.

The form of a $\Delta_{tr}H° = f(X_S)$ dependence is determined by the contributions of general and specific solvations of the solute. The enthalpy of the formation of a cavity in water is minimum.[9] Strengthening of the structure of an H_2O—S mixed solvent[9—11] at $0 < X_S < 0.2$ results in an increase in the enthalpy of the formation of a cavity in the solvent that corresponds to the size of a molecule of the solute. In this region of compositions, the contribution of specific solvation is of secondary importance. It can be said that in the region of small quantities of nonelectrolyte added to water, the shapes of $\Delta_{tr}H° = f(X_S)$ dependences are mostly determined by the energetics of formation of a cavity in the mixed solvent. It should be noted that this approach does not explain a number of discrepancies. To explain these, the variation of the electron-withdrawing ability of a mixture with varying its composition should also be taken into account. Water is one of the most strong acceptors of electrons. Therefore, the electron-withdrawing properties of mixtures of water with the majority of nonelectrolytes decrease as the proportions of nonaqueous components increase.[12] The energetics of specific interactions of electron-donating compounds (for example, DO) with the solvent should decrease in the same direction. This factor acts in the same direction as the contribution of the enthalpy of the formation of a cavity, and the combination of these factors governs the form of the $\Delta_{tr}H° = f(X_S)$ dependence in the region of small quantities of a nonelectrolyte added to water.

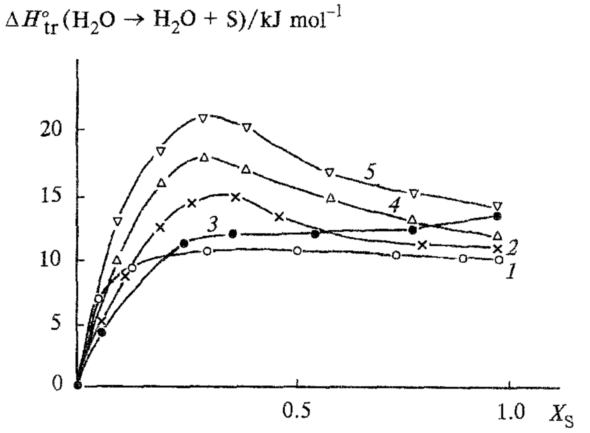

Fig. 1. Enthalpies of transfer ($\Delta_{tr}H°$) of 1,4-dioxane from water into H_2O—S mixtures, where S is acetone (*1*), DMSO (*2*), or MeOH (*3*), and $\Delta_{tr}H°$ of EtOAC (*4*) and Bu^{t}OAc (*5*) from water into an H_2O—DMSO mixture.

The more substantial increase in the endothermic nature of the transfer of DO into an H_2O—DMSO mixture compared to the H_2O—Me_2CO mixture in the $0.15 < X_S < 0.40$ interval is associated with a greater strengthening of the structure of the H_2O—DMSO mixed solvent. An endo maximum at $X_{DMSO} \approx 0.35$ for this mixture confirms the conclusion[10] that $(DMSO)_2 \cdot 2H_2O$ associates are formed and the structure of the mixture is maximally strengthened. The endo contribution from the formation of a cavity during solvation of DO is maximum at this composition, and when the proportion of DMSO in the mixture increases, this contribution decreases. At $X_{Me_2CO} > 0.15$, the $\Delta_{tr}H°$ values for DO practically do not depend on the composition of $H_2O—Me_2CO$ mixtures. It may be assumed that the decrease of the endo contribution from the cavity formation in the solvent is counterbalanced by the decrease in the exo contribution from the specific interaction of DO with the mixed solvent.

In the case of a more structurized solvent, greater energy consumption is required for the formation of cavities in which molecules of the solute could be arranged and also for increase in the size of the molecules of the dissolved compound. This probably accounts for the greater endothermic effect of the transfer of Bu^tOAc, compared with DO, into $H_2O—DMSO$ mixtures, while the donor and, apparently, acceptor properties of the compounds being dissolved are similar (see Table 2). The fact that the endothermic effect of the transfer of EtOAc is greater than that of DO cannot be explained in a similar way, since the sizes of their molecules are similar. The different values of $\Delta_{tr}H°$ for EtOAc and DO in $H_2O—DMSO$ mixtures are due to the difference in the specific solvation of these substances. The electron-donating properties of EtOAc are more pronounced than those of DO. A decrease in the electron-withdrawing properties of the $H_2O—DMSO$ mixture[12] results in a decrease in the exo contribution of the specific solvation of the substance whose electron-donating properties are more pronounced (EtOAc).

Figures 2 and 3 show the $\Delta_{tr}H° = f(X_S)$ dependences for PC and AN in $H_2O—S$ mixtures (S is DMSO, Me_2CO, and MeOH). The approach that we have used to consider analogous dependences for solutions of DO can also be used in this case. An increase in the endothermicity of the transfer of PC and AN in the region of small proportions of nonaqueous component is due to the fact that the endo contribution of the enthalpy of cavity formation in a mixed solvent predominates. From Figs. 2 and 3, it can also be seen that the $\Delta_{tr}H°$ values for solutions of PC or AN in a $H_2O—Me_2CO$ mixture increase more dramatically than those for solutions in $H_2O—DMSO$ system. This is probably due to the large energy consumption needed for the formation of a cavity in an $H_2O—Me_2CO$ mixture, *i.e.*, to the fact that the $H_2O—Me_2CO$ mixture is relatively more structurized in this region of concentrations.

It has been reported[11] that clathrate structures of variable composition, $xMe_2CO \cdot yH_2O$, stable in the $0 < X_{Me_2CO} < 0.15$ region, are formed. The mole fraction $X_{Me_2CO} \approx 0.15$ is a sort of a limiting concentration, after which the $\Delta_{tr}H°$ values for DO, as has been noted above (see Fig. 1), virtually do not depend on the composition of the mixture, while in the case of PC and AN, the $\Delta_{tr}H° = f(X_{Me_2CO})$ curves have extremum points at this composition of the mixture. The maximum of the endothermic effect at $X_{Me_2CO} \approx 0.15$ corresponds to greatest strengthening of the structure of this mixture. In the case of the $H_2O—DMSO$ system, the endo maxima for dissolved substances possessing various donor-acceptor properties are observed at the same composition of the mixture (*cf.* Figs. 1—3). In the region of medium compositions and also at high proportions of the nonaqueous component, an increase in the basicities[13] of $H_2O—DMSO$ and $H_2O—Me_2CO$ mixtures results in an increase of the exo contribution of specific solvation for electron-withdrawing compounds (AN or PC). The endo contribution from the enthalpy of the formation of a cavity in the mixed solvent also decreases in this range of concentrations, which is due to the decrease in the structurization of the mixtures. Both contributions act in the same direction. The fact that the dependences under consideration for PC are more steep than those for AN is probably caused by the difference between the sizes of their molecules.

In conclusion, note that an analysis of the solvation characteristics on quantitative grounds requires that they be divided into general and specific constituents. For this to be done, additional thermochemical data are needed.

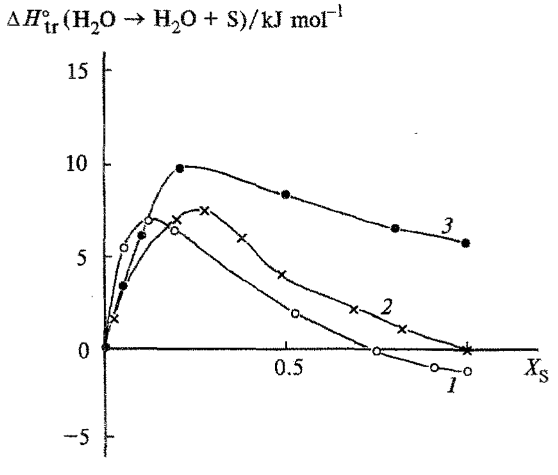

Fig. 2. Enthalpies of transfer of propylene carbonate from water into $H_2O—S$ mixtures, where S is acetone (*1*), DMSO (*2*), or MeOH (*3*).

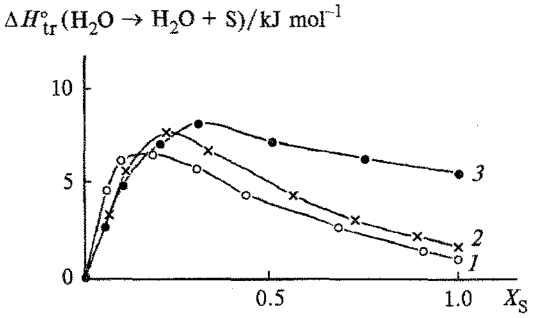

Fig. 3. Enthalpies of transfer of acetonitrile from water into $H_2O—S$ mixtures, where S is acetone (*1*), DMSO (*2*), or MeOH (*3*).

References

1. A. C. Rouw and G. Somsen, *J. Solut. Chem.*, 1981, **10**, 533.
2. A. C. Rouw and G. Somsen, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3397.
3. Yu. M. Kessler and A. L. Zaitsev, *Sol'vofobnye effekty* [*Solvophobic Effects*], Khimiya, Leningrad, 1989, (in Russian).
4. V. P. Korolev, D. V. Batov, V. N. Vandyshev, and O. A. Antonova, *Termodinamika rastvorov neelektrolitov* [*Thermodynamics of Solutions of Nonelectrolytes*], 1989, **1**, 13 (in Russian).
5. B. G. Cox, *J. Chem. Soc., Perkin Trans. 2*, 1973, 607.
6. A. Gordon and R. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, J. Wiley & Sons, New York—London, 1972.
7. A. Weissberger, E. Proskauer, and D. Riddick, *Organic Solvents, Physical Properties and Methods of Purification*, Ed. A. Weissberger, Interscience Publishers, New York, 1955.
8. D. V. Batov, Ph.D. (Chem.) Thesis, Institute of Chemistry of Non-Aqueous Solutions of the USSR Academy of Sciences, Ivanovo, 1987 (in Russian).
9. V. P. Belousov and M. Yu. Panov, *Termodinamika vodnykh rastvorov neelektrolitov* [*Thermodynamics of Aqueous Solutions of Nonelectrolytes*], Khimiya, Leningrad, 1983 (in Russian).
10. M. I. Shakhparonov and I. V. Chekalin, *Zh. Strukt. Khim.*, 1970, **11**, 599 [*J. Struct. Chem. USSR*, 1970, **11** (Engl. Transl.)].
11. C. M. Kinart, W. J. Kinart, and L. Skulski, *Pol. J. Chem.*, 1986, **41**, 4519.
12. U. Mayer, W. Gerger, and V. Gutmann, *Monatsh. Chem.*, 1977, **108**, 489.
13. T. M. Krygowski, P. K. Wrona, and U. Zielkowska, *Tetrahedron*, 1985, **41**, 4519.
14. V. Gutmann, *Coordination Chemistry in Non-Aqueuos Solutions*, Ed. V. Gutmann, Springer Verlag, Vienna—New York, 1968.
15. A. Bondy, *J. Phys. Chem.*, 1964, **63**, 441.

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