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Solvation of alcohols with different number of OH groups in mixed solvents H_2O—1,4-dioxane and H_2O—1,2-dimethoxyethane at 298.15 K

***M. V. Kulikov*[a]* *and E. Yu. Trutneva*[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 ul. F. Engel'sa, 153460 Ivanovo, Russian Federation.
Fax: 007 (093 2) 30 1826

The enthalpies of solution of *n*-propyl alcohol, ethylene glycol, and glycerol in the H_2O—1,4-dioxane and H_2O—1,2-dimethoxyethane mixtures were measured in the range of molal concentrations (m_{alc}) of the dissolved alcohol from 0 to 0.1 mol kg^{-1} at 298.15 K. The enthalpies of solvation of alcohols and the enthalpies of their transfer from water to a mixed aqueous-organic solvent were discussed. The effect of the nature of the studied nonelectrolytes on the characteristics obtained was established. The enthalpy coefficients of binary (h_{23}) and ternary (h_{223}) interactions between the molecules of the solute (subscript 3) and the non-aqueous component (subscript 2) of the mixed solvent in the ternary solution were calculated. The h_{23} values increase as hydrophobic properties in the alcohol series (glycerol, ethylene glycol, and *n*-propyl alcohol) increase.

Key words: *n*-propyl alcohol, ethylene glycol, glycerol; 1,4-dioxane, 1,2-dimethoxyethane; water, mixed solvents; enthalpy of solution, enthalpy of solvation, enthalpy of transfer; solvophobic (hydrophobic) properties; binary and ternary interactions, enthalpy coefficients.

Aqueous solutions of monatomic and polyatomic alcohols have been studied in considerable detail.[1–3] However, only a few data on enthalpies of solution of both mono- and polyatomic alcohols in individual non-aqueous and mixed solvents have been reported. In this work, solvation of mono-, di-, and triatomic alcohols (*n*-propyl alcohol, ethylene glycol, and glycerol, respectively) in mixtures of water with 1,4-dioxane and 1,2-dimethoxyethane (cyclic and aliphatic C_4-diether, respectively) was studied and parameters characterizing the intermolecular interactions in solution were determined.

Experimental

n-Propyl alcohol (PrOH), ethylene glycol (EG), and glycerol (GL) of chromatographic grade were used. 1,4-Dioxane (1,4-DO) and 1,2-dimethoxyethane (1,2-DME) were tested for peroxide admixtures and purified using the previously recommended procedure[4] with sampling the medium fraction. Titration with the Fischer reagent[5] showed that the water content in alcohols and ethers did not exceed 0.06 wt.% and 0.02 wt.%, respectively.

Aqueous-ethereal mixtures were prepared by gravimetric method with an accuracy of 0.001 mole fraction using freshly distilled water (bidistilled water with a specific conductivity of $1 \cdot 10^1\ \Omega^{-1}\ cm^{-1}$).

The enthalpies of solution were measured on an isothermic-shell ampule microcalorimeter. The volume of the reaction vessel was 65 cm^3. The measurements were carried out at 298.15 K, and temperature was kept constant with an accuracy of ±0.0002 K. The concentrations of the solute did not exceed 0.1 mol per 1 kg of the solvent. The thermal effects of dissolution of alcohols were shown to be independent of their concentrations within the limits of experimental error. For this reason, the arithmetic mean values of thermal effects of dissolution ($\Delta_{sol}H^m$) were taken as the standard enthalpies of solution ($\Delta_{sol}H^\circ$) (Table 1, 2).

Results and Discussion

Solvation of alcohols. The enthalpies of solvation ($\Delta_s H^\circ$), characterizing the process of the transfer of the solute from the gas phase to the solvent in question and containing no contribution of intermolecular interactions from the condensed state, were calculated using the enthalpies of solution ($\Delta_{sol}H^\circ$) and vaporization ($\Delta_{vap}H^\circ$) of the substances:

$$\Delta_s H^\circ = \Delta_{sol} H^\circ - \Delta_{vap} H^\circ. \qquad (1)$$

The $\Delta_{vap}H^\circ$ values of 44.01, 47.5, 67.7, 91.7, 36.8, and 36.4 kJ mol^{-1} were used for H_2O,[6] PrOH,[7] EG,[8] GL,[9] 1,4-DO,[7] and 1,2-DME,[7] respectively. The rela-

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Table 1. Experimental ($\Delta_{sol}H^m$) and standard ($\Delta_{sol}H^\circ$) enthalpies of solution (in kJ mol^{-1}) of mono-, di-, and triatomic alcohols in the H_2O—1,4-dioxane mixture at 298.15 K

X	*n*-Propyl alcohol		Ethylene glycol		Glycerol	
/mole fraction	$m \cdot 10^2$	$\Delta_{sol}H^m$ [$\Delta_{sol}H^\circ$]	$m \cdot 10^2$	$\Delta_{sol}H^m$ [$\Delta_{sol}H^\circ$]	$m \cdot 10^2$	$\Delta_{sol}H^m$ [$\Delta_{sol}H^\circ$]
0	6.87	−10.15	5.55	−6.94	5.44	−5.55
	7.12	−10.11	6.75	−6.80	6.65	−5.43
		[−10.13±0.01]		[−6.87±0.07]		[−5.49±0.06]
0.001	5.43	−10.14	5.82	−6.68	4.95	−5.49
	6.79	−10.04	7.13	−6.74	5.84	−5.41
		[−10.03±0.07]		[−6.71±0.03]		[−5.45±0.04]
0.002	5.24	−9.98	4.48	−6.74	4.72	−5.45
	5.99	−10.10	6.53	−6.80	6.43	−5.39
		[−10.03±0.07]		[−6.77±0.03]		[−5.42±0.03]
0.003	6.18	−9.33	4.55	−6.86	6.43	−5.30
	6.44	−9.41	5.85	−6.70	7.01	−5.38
		[−9.37±0.04]		[−6.78±0.08]		[−5.34±0.04]
0.006	5.14	−8.50	4.97	−5.95	4.92	−5.19
	6.43	−8.62	5.88	−6.05	6.53	−5.23
		[−8.56±0.06]		[−6.00±0.05]		[−5.21±0.02]
0.010	5.88	−7.56	6.51	−6.16	5.73	−4.27
	6.12	−7.44	7.23	−6.10	6.35	−4.33
		[−7.50±0.06]		[−6.13±0.03]		[−4.30±0.03]
0.030	6.79	−7.17	5.94	−4.64	5.64	−3.41
	7.12	−7.03	6.54	−4.60	6.53	−3.51
		[−7.10±0.07]		[−4.62±0.02]		[−3.46±0.05]
0.033	5.66	−5.36				
	6.42	−5.30				
		[−5.33±0.03]				
0.040			5.86	−4.26	6.42	−2.73
			5.94	−4.14	7.36	−2.79
				[−4.20±0.06]		[−2.76±0.03]
0.050	5.32	−4.57	5.89	−3.70	4.84	−2.70
	5.94	−4.49	6.83	−3.84	7.02	−2.76
		[−4.53±0.04]		[−3.77±0.07]		[−2.73±0.03]
0.061	4.54	−3.60			5.82	−2.49
	5.69	−3.66			6.45	−2.41
		[−3.63±0.03]				[−2.45±0.04]
0.070	6.75	−1.87	4.87	−3.00	5.55	−2.19
	7.11	−1.79	6.96	−3.08	7.01	−2.23
		[−1.83±0.04]		[−3.04±0.04]		[−2.21±0.02]
0.100	5.44	−0.20	5.63	−2.21	5.46	−1.40
	6.82	−0.10	7.23	−2.11	7.42	−1.30
		[−0.15±0.05]		[−2.16±0.05]		[−1.35±0.05]
0.200	5.91	1.46	5.87	−0.59	4.93	−0.24
	7.23	1.56	6.93	−0.65	6.35	−0.18
		[1.51±0.05]		[−0.62±0.03]		[−0.21±0.03]
0.300	5.82	2.47	5.75	−0.14	5.52	0.17
	7.26	2.33	6.82	−0.10	7.53	0.25
		[2.40±0.07]		[−0.12±0.02]		[0.21±0.04]
0.500	5.73	3.16	5.77	0.67	4.74	0.73
	6.47	3.04	6.75	0.61	7.43	0.79
		[3.10±0.06]		[0.64±0.03]		[0.76±0.03]
0.750	4.84	4.52	5.86	2.02	5.46	1.99
	6.55	4.60	6.83	2.16	6.92	1.91
		[4.56±0.04]		[2.09±0.07]		[1.95±0.04]
0.900	5.06	5.47	5.63	3.93	4.42	3.85
	6.84	5.53	6.48	3.87	5.78	3.80
		[5.50±0.03]		[3.90±0.03]		[3.82±0.03]
1.000	4.82	6.96	5.84	7.82	4.87	7.76
	6.76	7.04	7.27	7.90	6.32	7.66
		[7.00±0.04]		[7.86±0.04]		[7.71±0.05]

Note. Here and in Table 2 m/mol kg^{-1} is the molality of the alcohol solution, and X is the mole fraction of the nonaqueous component of the solvent.

Table 2. Experimental ($\Delta_{sol}H^m$) and standard ($\Delta_{sol}H^\circ$) enthalpies of solution (in kJ mol^{-1}) of mono-, di-, and triatomic alcohols in the H_2O—1,2-dimethoxyethane mixture at 298.15 K

X	n-Propyl alcohol		Ethylene glycol		Glycerol	
/mole fraction	$m\cdot10^2$	$\Delta_{sol}H^m$ [$\Delta_{sol}H^\circ$]	$m\cdot10^2$	$\Delta_{sol}H^m$ [$\Delta_{sol}H^\circ$]	$m\cdot10^2$	$\Delta_{sol}H^m$ [$\Delta_{sol}H^\circ$]
0	5.94	−10.16	4.55	−6.76	6.94	−5.56
	6.71	−10.10	4.97	−6.84	7.15	−5.44
		[−10.13±0.03]		[−6.80±0.04]		[−5.50±0.06]
0.001	4.66	−10.11	5.11	−6.74	4.54	−5.43
	5.90	−10.03	5.87	−6.70	5.72	−5.49
		[−10.07±0.04]		[−6.72±0.02]		[−5.46±0.03]
0.002	4.17	−9.46	5.48	−6.57	4.69	−5.49
	4.83	−9.54	6.27	−6.63	4.72	−5.39
		[−9.50±0.04]		[−6.60±0.03]		[−5.44±0.05]
0.003	5.21	−9.81	4.17	−6.34	5.02	−5.47
	5.24	−9.93	4.66	−6.26	5.59	−5.45
		[−9.87±0.06]		[−6.30±0.04]		[−5.46±0.01]
0.007	5.05	−9.23			6.13	−5.01
	5.94	−9.37			7.22	−5.09
		[−9.30±0.07]				[−5.05±0.04]
0.008			5.81	−6.17		
			6.77	−6.23		
				[−6.20±0.03]		
0.015	4.69	−7.80	5.22	−5.34	4.52	−4.88
	5.23	−7.70	5.78	−5.28	5.67	−4.94
		[−7.75±0.05]		[−5.31±0.03]		[−4.91±0.03]
0.020	4.24	−7.82			5.70	−3.73
	5.77	−7.76			6.36	−3.67
		[−7.79±0.03]				[−3.70±0.03]
0.025	5.19	−4.23	4.71	−4.46	4.76	−1.97
	6.85	−4.19	4.88	−4.44	5.43	−1.81
		[−4.21±0.02]		[−4.45±0.01]		[−1.89±0.08]
0.035			5.15	−3.70		
			5.78	−3.78		
				[−3.74±0.04]		
0.038	4.97	−4.41			5.39	−2.14
	5.14	−4.35			6.38	−2.02
		[−4.38±0.03]				[−2.08±0.06]
0.040			5.28	−3.32		
			6.32	−3.28		
				[−3.30±0.03]		
0.050	5.20	−2.19	4.88	−2.82	6.65	−1.27
	5.61	−2.11	4.97	−2.70	6.87	−1.23
		[−2.15±0.04]		[−2.76±0.06]		[−1.25±0.02]
0.060			5.55	−1.90		
			6.17	−1.82		
				[−1.86±0.04]		
0.075			5.45	−1.33		
			5.94	−1.21		
				[−1.27±0.06]		
0.077	5.06	−0.10			5.43	−0.12
	6.02	−0.24			6.82	−0.20
		[−0.17±0.07]				[−0.16±0.04]

(*to be continued*)

Table 2 (*continued*)

X /mole fraction	*n*-Propyl alcohol		Ethylene glycol		Glycerol	
	$m \cdot 10^2$	$\Delta_{sol}H^m$ [$\Delta_{sol}H^\circ$]	$m \cdot 10^2$	$\Delta_{sol}H^m$ [$\Delta_{sol}H^\circ$]	$m \cdot 10^2$	$\Delta_{sol}H^m$ [$\Delta_{sol}H^\circ$]
0.090			5.96	−0.78		
			6.84	−0.70		
				[−0.74±0.04]		
0.100	4.31	2.63	5.81	−0.44	5.91	0.09
	4.87	2.71	7.24	−0.56	6.28	−0.01
		[2.67±0.04]		[−0.50±0.06]		[0.04±0.05]
0.0150			5.74	−0.02		
			6.95	−0.10		
				[−0.06±0.04]		
0.200					5.51	0.41
					6.63	0.47
						[0.44±0.03]
0.300	4.84	3.45	5.69	−0.76	4.97	−0.11
	5.13	3.51	6.31	−0.70	5.24	−0.19
		[3.48±0.03]		[−0.73±0.03]		[−0.15±0.04]
0.500	4.49	2.50	5.18	−0.87	4.85	−0.64
	5.19	2.42	7.14	−0.91	5.72	−0.76
		[2.46±0.04]		[−0.89±0.02]		[−0.70±0.06]
0.750	5.27	1.15	6.14	−0.75	4.86	−0.73
	5.24	1.03	6.99	−0.81	6.73	−0.81
		[1.09±0.06]		[−0.78±0.03]		[−0.77±0.04]
0.900	5.28	1.53	4.71	0.25	5.84	0.17
	5.88	1.43	7.19	0.35	6.94	0.11
		[1.48±0.05]		[0.30±0.05]		[0.14±0.03]
1.000	4.32	2.23	4.55	1.97	5.71	2.10
	4.89	2.33	5.64	2.03	5.89	2.02
		[2.28±0.05]		[2.00±0.03]		[2.06±0.04]

tive partial molar enthalpies of solution of water (Eq. (2)), 1,4-DO,[10,11] and 1,2-DME[12] (Eq. (3)) were calculated from the dependence $H^E = f(X_2)$ approximated by the Redlich—Kister equation (Eq. (4)).

$$\bar{h}_1^0 = H^E - X_2\left(dH^E/dX_2\right) \tag{2}$$

$$\bar{h}_2^0 = H^E + X_1\left(dH^E/dX_2\right) \tag{3}$$

$$H^E = X_2(1-X_2)\cdot\sum_{i=1}^{n} A_i(1-2X_2)^i \tag{4}$$

Hereafter subscript 1 is referred to water while subscript 2 is referred to the organic cosolvent. The coefficients of Eq. (4) are given in Table 3.

The enthalpies of solvation are the sum of the endoeffect of the formation of a cavity in the solvent and of the exoeffect of nonspecific and specific "solute—solvent" interactions. As can be seen in Figs. 1 and 2, solvation of alcohols in both mixed solvents studied increases on going from PrOH to EG and GL, *i.e.*, as the number of hydroxyl groups in the alcohol molecule increases. It should be noted that adding one more hydroxyl group in the alcohol molecule makes a constant contribution of 21 kJ mol^{-1} to the enthalpy of solvation for both mixed solvents. An increase in exothermicity of the $\Delta_s H^\circ$ values in the series PrOH, EG, and GL also persists when these alcohols are dissolved in other mixed aqueous-organic solvents (for instance,

Table 3. The coefficients of Eq. (4) for mixtures of water with 1,4-dioxane

Coefficient	I	II	III
A_0	0.811	0.497	−1.486
A_1	−3.630	−3.755	−3.945
A_2	−1.967	−2.132	−5.977
A_3	−4.109	−4.357	−11.177
r^2	0.992	0.998	0.994
S	0.50	0.14	0.52

Note. I, II, and III correspond to data taken from Refs. 10, 11, and 12, respectively.

H_2O—MeOH[13] and H_2O—Bu^{t}OH[14]). The solvation of each of the alcohols dissolved in the mixture of water with cosolvents increases in the sequence 1,4-DO, MeOH, 1,2-DME, Bu^{t}OH. The donor numbers of these compounds increase in the same sequence: DN/kJ mol^{-1} = 14.8 (1,4-DO), 19.0 (MeOH),[15] 23.9 (1,2-DME), and 57.0 (Bu^{t}OH).[16]

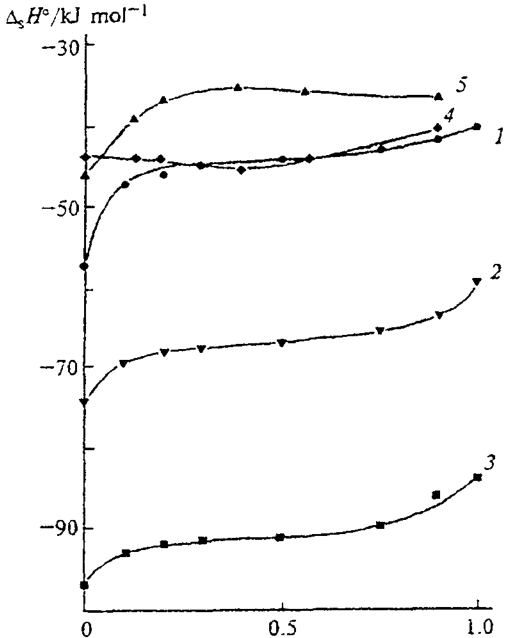

Fig. 1. Enthalpies of solvation of *n*-propyl alcohol (*1*), ethylene glycol (*2*), glycerol (*3*), water (*4*), and 1,4-dioxane (*5*) in the H_2O—1,4-dioxane mixture.

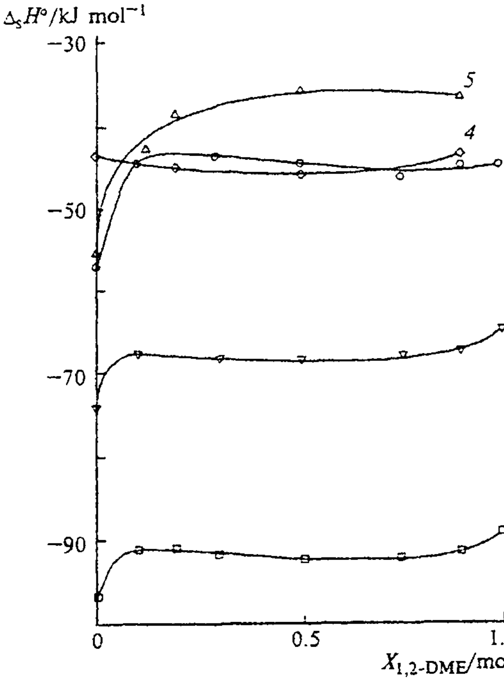

Fig. 2. Enthalpies of solvation of *n*-propyl alcohol (*1*), ethylene glycol (*2*), glycerol (*3*), water (*4*), and 1,2-dimethoxyethane (*5*) in the H_2O—1,2-dimethoxyethane mixture.

The effect of composition of the mixture on the solvation of the substances is clearly demonstrated by the concentration dependences of the enthalpies of transfer ($\Delta_{tr}H°$). The $\Delta_{tr}H°$ values characterize changes in the enthalpy of solvation of the solute in the mixed water—nonelectrolyte (NE) solvent ($\Delta_{sol}H°(H_2O+NE)$) as compared with the enthalpy of its hydration ($\Delta_{sol}H°(H_2O)$) and are calculated using Eq. (5).

$$\Delta_{tr}H°(H_2O \rightarrow H_2O+NE) = \Delta_{sol}H°(H_2O+NE) - \Delta_{sol}H°(H_2O) \quad (5)$$

The type of the dependence $\Delta_{tr}H° = f(X_2)$ (Figs. 3 and 4) is dependent on the contributions of the nonspecific and specific solvation of the solute. Strengthening of the structure of the mixed solvents in the $0 < X_2 < 0.2$ mole fraction interval[7] results in increasing the enthalpy of the cavity formation in the solvent. The contribution from the endothermic nonspecific solvation dominates over the contribution from the exothermic specific solvation in this composition range of the mixtures of alcohol and ether solutions, and the type of the dependence $\Delta_{tr}H° = f(X_2)$ is mainly dependent on the energetics of the cavity formation in a mixed solvent. The

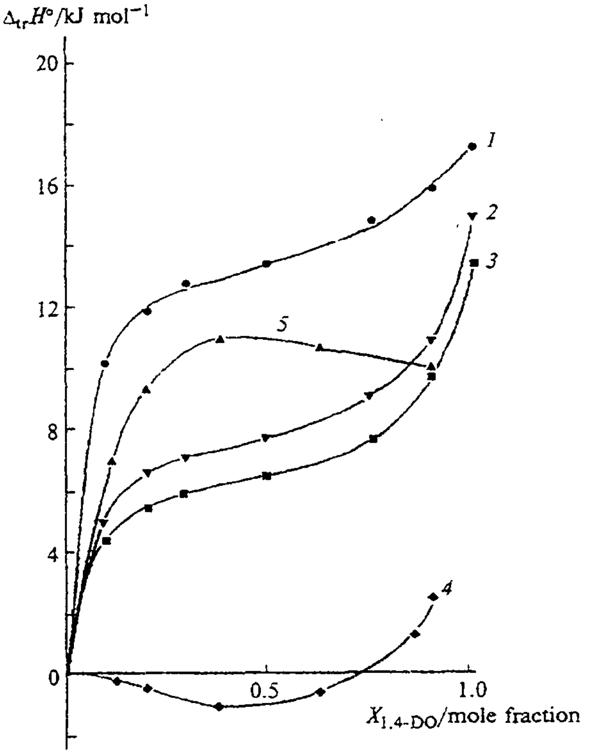

Fig. 3. Enthalpies of transfer of *n*-propyl alcohol (*1*), ethylene glycol (*2*), glycerol (*3*), water (*4*), and 1,4-dioxane (*5*) in the H_2O—1,4-dioxane mixture.

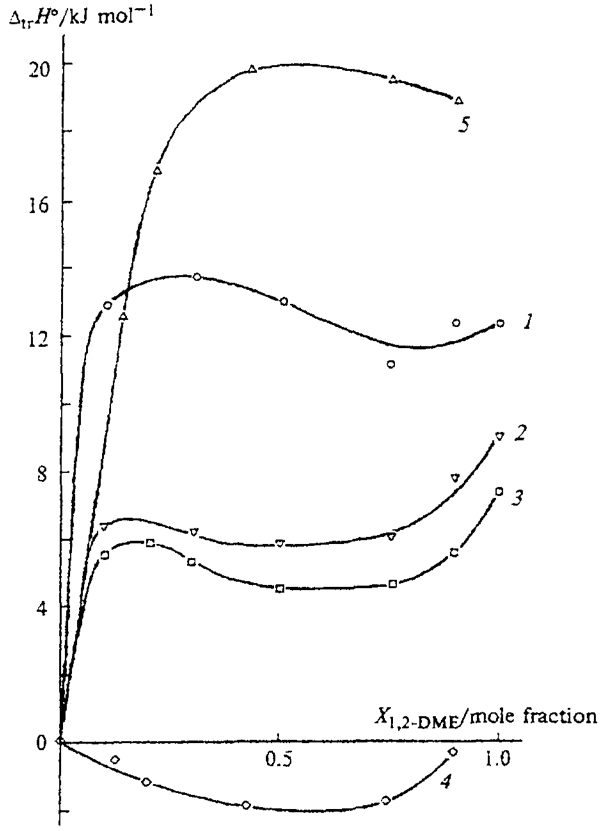

Fig. 4. Enthalpies of transfer of *n*-propyl alcohol (*1*), ethylene glycol (*2*), glycerol (*3*), water (*4*), and 1,2-dimethoxyethane (*5*) in the H_2O—1,2-dimethoxyethane mixture.

more appreciable increase in the $\Delta_{tr}H°$ values for alcohols in the H_2O—1,2-DME mixture in the $0 < X_2 < 0.2$ mole fraction interval is associated with higher degree of structurization of the given system as compared to the H_2O—1,4-DO mixture.[7] An increase in the proton-donor properties on going from PrOH to EG and further to GL leads to the strengthening of specific interactions of the alcohol molecules with the components of mixed solvents. A competition between the contributions from the exothermic specific solvation and from the endothermic nonspecific solvation (with predominance of the latter) is observed in the H_2O—1,4-DO mixture as the ether content in a mixed solvent increases ($X_2 > 0.2$ mole fraction). In the H_2O—1,2-DME mixture, these contributions counterbalance each other in the 0.3 mole fraction $< X_2 <$ 0.7 mole fraction interval, and the solvation of alcohols remains nearly unchanged in the indicated composition range. At $X_2 > 0.7$ mole fraction, a new increase in endothermicity of the $\Delta_{tr}H°$ values is observed in the system in question.

Intermolecular interactions. Experimental data on the properties of aqueous solutions of substances accumulated to date allowed one to select a number of parameters for comparing their hydrophobic behavior.[17—19] The most appropriate among them is the derivative of the second virial coefficient with respect to pressure $(dB_{22}/dp)_T$.[19] The $(dB_{22}/dp)_T$ value is positive for hydrophilic substances and negative for hydrophobic substances, and its absolute value increases as their hydrophobicity increases. However, it is often difficult to calculate the $(dB_{22}/dp)_T$ derivative because of a lack of necessary experimental data.[19]

Quantitative information on the hydrophobic effects can also be obtained by processing the data on various thermodynamic properties of the solutions using the McMillan—Mayer theory.[20] In this case, the coefficients of binary, ternary, and other multiple interactions of the solute molecules with each other are usially determined, and a comparative analysis is performed without interpreting their values.

As was noted in a number of works,[17—19,21] the enthalpy coefficients of binary interactions (h_{22}) for aqueous solutions of substances can be used as a criterion for hydrophobic behavior of these compounds in water. The values of $(dB_{22}/dp)_T$ as well as the enthalpy (h_{22}) and Gibbs (g_{22}) coefficients of binary interaction of the molecules of certain nonelectrolytes in water are listed in Table 4. It follows from the extensive data on the coefficients of multiple (in particular binary) interactions[17—19,21] that the h_{22} values for aqueous solutions of hydrophobic substances are positive and increase as the number of hydrophobic groups in the molecules of dissolved compounds increases. The h_{22} coefficients for hydrophilic substances are, as a rule, negative. However, unlike $(dB_{22}/dp)_T$, the h_{22} values do not always adequately reflect the degree of hydrophobicity of the substance.[18,19]

The coefficients of interactions of the molecules of different types (h_{ij}, h_{ijk}, *etc.*) can be determined in ternary solutions; however, the structure of the *h* coefficients becomes much more complicated.[19] When the functions of the transfer of one component from its aqueous solution to a binary solvent are used, the following equality is valid:

$$h_{ij} = h_{22}. \tag{6}$$

Using experimental data (see Tables 1 and 2) and Eq. (7),[22] we calculated the enthalpy coefficients of binary (h_{23}) and ternary (h_{223}) interactions of the solute molecule (alcohol, subscript 3) with the molecules of the nonaqueous component of the solvent (ether, subscript 2) in a mixed solvent:

$$\Delta_{tr}H°(H_2O \rightarrow H_2O\text{+NE}) = h_{23} \cdot m + h_{223} \cdot m^2 + ..., \tag{7}$$

where *m*/mol kg^{-1} is the molal concentration of the nonelectrolyte in a mixed solvent.

The results obtained are presented in Table 5. This table also contains the h_{23} and h_{223} values for solutions of PrOH, EG, and GL in mixtures of water with MeOH,[23] acetone (Me_2CO),[24] DMF,[25] and Bu^{t}OH [23] calculated using published data.

Table 4. The values of the enthalpy (h_{22}/J kg mol^{-2}) and Gibbs (g_{22}/J kg mol^{-2})[7] coefficients of binary interactions, $(dB_{22}/dp)_T$/cm^3 mol^{-1} bar^{-1},[19] donor (DN_{SbCl_5}/kJ mol^{-1}),[16] and acceptor (AN/kJ mol^{-1})[16] numbers of nonelectrolytes in aqueous solutions

Parameter	MeOH	EtOH	PrOH	EG	GL	DO	DME	DMF	Me$_2$CO	Bu^{t}OH
h_{22}	224 [26]	250 [26]	557 [26]	362 [27]	251 [27]	739 [7]	1095 [7]	737 [19]	770 [19]	656 [7]
g_{22}	−52	−125	−198	15	43	—	—	−106	—	−272
$(dB_{22}/dp)_T \cdot 10^2$	—	—	—	—	—	−0.8	—	−1.8	−1.2	—
DN_{SbCl_5}	19.1	19.2	19.8	20.0	19.0	14.8	23.9	26.6	17.0	57.0
AN	41.3	37.1	35.0	39.0	—	10.8	10.0	16.0	12.5	—

Table 5. The enthalpy coefficients of binary (h_{23}/J kg mol^{-2}) and ternary (h_{223}/J kg^2 mol^{-3}) interactions of alcohols with ethers in aqueous solutions

Non-electrolyte	PrOH		EG		GL		MeOH		EtOH	
	h_{23}	h_{223}	h_{23}	h_{223}	h_{23}	h_{223}	h_{23}	h_{223}	h_{23}	h_{223}
1,4-DO	1611	−83	1564	−116	1428	−123	—	—	—	—
1,2-DME	3630	−168	2026	−122	2381	−207	—	—	—	—
Me$_2$CO	2616	−140	1349	−80	1104	−59	—	—	—	—
MeOH	989	−14	760	−17	875	−30	—	—	—	—
Bu^{t}OH	—	—	2748	−324	2736	−338	—	—	—	—
DMF	2215	−66	—	—	—	—	1163	−40	1590	−26

As can be seen in Tables 4 and 5, the enthalpy coefficients of binary interactions of the molecules of the investigated alcohols in water with each other and those of the alcohol molecules and the nonaqueous component of the mixed aqueous-organic solvent are of the same order of magnitude. This is evidence of the close energies of hydrophobic hydration in the indicated solvents.

Binary association ($g_{22} < 0$) is known to be favorable for aqueous solutions of monatomic alcohols.[7] The h_{22} coefficients are positive and increase in the sequence MeOH < EtOH < PrOH, *i.e.*, as the number of hydrophobic groups in the alcohol molecule increases (see Table 3). It is assumed that the molecules of monatomic alcohols in their aqueous solutions interact with each other mainly through hydrocarbon radicals rather than through H-bonds.[7] The binary association for EG and GL is thermodynamically unfavorable ($g_{22} > 0$). It is hindered by the formation of numerous H-bonds with water[7]. However, the h_{22} values for these alcohols are also positive, which allows one to categorize them as hydrophobic substances (since no data on their $(dB_{22}/dp)_T$ values are available). As can be seen from Table 3, the values of the h_{22} coefficients increase in the sequence GL < EG < PrOH. The hydrophobic properties of these substances also increase in the same sequence.

For ternary systems, the standard enthalpies of transfer $\Delta_{tr}H°(H_2O \rightarrow H_2O+NE)$ for small additives of nonaqueous component (nonelectrolyte, $X_2 \leq 0.1$ mole fraction) are determined by the coefficients of binary interactions h_{23}.[19] As follows from the data in Table 4, the values of the h_{23} coefficients for the solutions of the studied alcohols in mixtures of water with nonelectrolytes of different chemical nature increase, as a rule, in the sequence GL, EG, PrOH (for monatomic alcohols, MeOH < EtOH < PrOH in a H_2O—DMF mixture), *i.e.*, as the hydrophobic properties of the substances increase. It seems likely that the molecules of alcohol and those of the nonaqueous component of the mixed solvent in the ternary systems also interact mainly through the hydrocarbon radicals. The molecules of the solute and cosolvent interacting in an aqueous solution are known to form a common hydrate shell and jointly affect the state of the surrounding molecules of water, thus strengthening or destroying its structure.[19] The increase in the enthalpy coefficients in the sequence MeOH, EtOH, and PrOH for alcohols dissolved in water (h_{22}) and in the H_2O—DMF mixture (h_{23}), as well as that observed on going from GL to EG and further to PrOH in the H_2O+NE mixtures (h_{23}), is associated with differences in the hydrophobic and electron-donor properties of alcohols and nonelectrolytes (see Table 3). For instance, the h_{22} coefficients increase in the following series of cosolvents: MeOH < Me$_2$CO < 1,4-DO < 1,2-DME < Bu^{t}OH, *i.e.*, their hydrophobic properties increase. The h_{23} coefficients for solutions of alcohols in mixtures of water with the above cosolvents increase in the same sequence. A parallel change in the h_{23} and h_{22} coefficients (and hence, to a certain extent, in $(dB_{22}/dp)_T$) allows us to conclude that the h_{23} value can be used as a criterion for hydrophobicity of substances in ternary systems in the absence of a more reliable criterion.

However, it is very difficult to unambiguously interpret the mechanism of intermolecular interactions for ternary systems using the h_{23} coefficients (as in the case of binary aqueous solutions) because of uncertainty in the interpretation of the obtained coefficients and scarce available information.

The coefficients of ternary interactions (h_{223}) for the systems studied have opposite signs and are an order of magnitude lower as compared to the coefficients of binary interactions (h_{23}). They have an appreciable effect on the character of the dependences $\Delta_{tr}H^\circ(H_2O \rightarrow H_2O+NE) = f(X_2)$ in the range of medium concentrations of the nonaqueous component in the mixed solvent. However, concepts on the dominant role of the hydrophobic effects lose meaning in this composition range.

At present it is impossible to reliably predict the character of the dependence $\Delta_{tr}H^\circ(H_2O \rightarrow H_2O+NE) = f(X_2)$ using the values and signs of the coefficients h_{23} and h_{223}. However, it is believed that if the nonelectrolyte is highly hydrophobic when the solute is transferred from water to the H_2O+NE mixture, one should expect an extremum dependence $\Delta_{tr}H^\circ(H_2O \rightarrow H_2O+NE) = f(X_2)$.[19] Extrema of this dependence also can be due to high hydrophobicity of the solute itself. Based on these assumptions, one can explain the character of dependences $\Delta_{tr}H^\circ(H_2O \rightarrow H_2O+NE) = f(X_2)$ for the solutions of alcohols in the H_2O—1,2-DME mixture (judging from the h_{22} value, 1,2-DME is a substance of medium hydrophobicity; therefore, the maxima on the indicated curve are weakly pronounced) and for PrOH in the H_2O—1,4-DO mixture (PrOH also is a substance of medium hydrophobicity).

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