Russian Journal of General Chemistry, Vol. 74, No. 5, 2004, pp. 663–666. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 5, 2004, pp. 725–728.

Energetics of Solvation of Mono- and Polyhydric Alcohols with Mixtures of Water with Acetone

D. V. Batov, A. V. Kustov, and V. P. Korolev

Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia

Received December 10, 2001

Abstract—In the cases of 1-propanol, 1,2-ethanediol, and 1,2,3-propanetriol in water–acetone mixtures at 298.15 K, the structures and properties of alcohols substantially affect the enthalpies of their solvation and only slightly affect the enthalpies of their transfer from water to the mixed solvent. As the composition of the mixed solvent is varied, a compensation of changes in nonspecific and specific solvation of alcohols containing equal numbers of nonpolar and polar fragments (methanol, 1,2-ethanediol, and 1,2,3-propanetriol) is observed.

Solvation of reagents to a large extent determines the thermodynamics and kinetics of chemical reactions in solutions. Therefore, data on the thermodynamics of solvation of substances in mixed solvents are necessary for predicting the reactivity of compounds. Studies in this field have been carried out over several years. We can point out the thermochemical studies of solvation of phenols and carboxylic acids [1, 2], aimed at elucidation of the effect of reagent solvation with water–alcohol solvents on the thermodynamics of acid–base equilibria. In the research on complex formation in aqueous-organic mixtures, Sharnin [3] has studied solvation of certain ligands (ethylenediamine, pyridine, 2,2'-bipyridyl, etc.). Thermodynamic data are available, according to which the additivity of the contributions of functional groups into the enthalpies, entropies and Gibbs energies of hydration of diols and triols is not obeyed [4, 5]. Solvation of polyhydric alcohols in mixed solvents has scarcely been studied. We have studied solvation of ethylene glycol and glycerol in water–methanol [6] and water–2-methyl-2-propanol mixed solvents [7]. It seemed important to study the effect on solvation of alcohols in mixtures of water with aprotic solvents of the number of hydroxy groups in the alcohol and the composition and properties of the mixed solvent. Therefore, in this work we measured the enthalpies of solution of 1-propanol (PrOH), 1,2-ethanediol [$(CH_2OH)_2$], and 1,2,3-propanetriol [$C_3H_5(OH)_3$] in mixtures of water with acetone (Me_2CO) at 298.15 K.

The experimental solution enthalpies are given in Tables 1 and 2. Using these data and the vaporization enthalpies of PrOH (47.48 kJ mol^{-1} [8]), $(CH_2OH)_2$ (61.10 kJ mol^{-1} [8]), and $C_3H_5(OH)_3$ (85.80 kJ mol^{-1} [8]), we calculated the solvation enthalpies of the compounds under study by Eq. (1).

$$\Delta H^0_{\mathrm{solv}} = \Delta H^0_{\mathrm{sol}} - \Delta H^0_{\mathrm{vap}}. \tag{1}$$

Table 1. Heat effects of solution (kJ mol^{-1}) of Pr(OH), $(CH_2OH)_2$, and $C_3H_5(OH)_3$ in H_2O–Me_2CO mixtures at 298.15 K[a]

X_2	PrOH		$(CH_2OH)_2$		$C_3H_5(OH)_3$	
	$m \times 10^4$	$\Delta H^m_{\mathrm{sol}}$	$m \times 10^4$	$\Delta H^m_{\mathrm{sol}}$	$m \times 10^4$	$\Delta H^m_{\mathrm{sol}}$
0	6.71	–10.19	4.55	–6.57	6.65	–5.67
	5.94	–10.14	4.97	–6.65	5.44	–5.79
0.033	4.23	–6.51	5.32	–4.94[b]	4.98	–4.71[c]
	4.68	–6.63	6.14	–5.02[b]	5.68	4.79[c]
0.05	4.87	–4.61	5.07	–3.68	5.39	–3.26
	4.99	–4.71	5.64	–3.76	5.82	–3.32
0.10	3.99	–0.35	5.36	–2.17	3.59	–1.20
	4.08	–0.47	6.14	–2.23	4.61	–1.28
0.15	4.56	1.15	5.54	–1.15	5.81	–0.64
	4.83	1.26	5.82	–1.27	5.93	–0.76
0.30	5.13	2.82	5.41	–0.17	5.63	0.82
	5.68	2.92	6.06	–0.25	5.90	0.92
0.50	5.61	3.15	6.54	–0.42	4.68	1.39
	5.72	3.27	6.99	–0.52	5.06	1.47
0.75	5.09	3.49	6.03	1.49	5.32	3.12
	5.41	3.59	6.12	1.57	5.96	3.18
0.90	6.14	3.58	3.89	4.45	4.67	5.95
	6.38	3.68	4.65	4.57	4.95	6.07
1.00	5.67	4.58	5.74	7.52	5.38	10.39
	5.83	4.70	5.86	7.62	6.14	10.45

[a] The dimension of m is mol of solute per 1000 g of solvent. [b] X_2 0.027. [c] X_2 0.021.

Table 2. Standard enthalpies of solution (kJ mol^{-1}) of Pr(OH), $(CH_2OH)_2$, and $C_3H_5(OH)_3$ in H_2O–Me_2CO mixtures at 298.15 K

X_2	PrOH		$(CH_2OH)_2$		$C_3H_5(OH)_3$	
	ΔH^0_{sol}	*se*, kJ mol^{-1}	ΔH^0_{sol}	*se*, kJ mol^{-1}	ΔH^0_{sol}	*se*, kJ mol^{-1}
0	–10.17	0.02	–6.61	0.04	–5.73	0.06
0.033	–6.57	0.06	–4.98[a]	0.04	–4.75[b]	0.04
0.05	–4.66	0.05	–3.72	0.04	–3.29	0.03
0.10	–0.41	0.06	–2.20	0.03	–1.24	0.04
0.15	1.21	0.06	–1.21	0.06	–0.70	0.06
0.30	2.87	0.05	–0.21	0.04	0.87	0.05
0.50	3.21	0.06	–0.47	0.05	1.43	0.04
0.75	3.54	0.05	1.53	0.04	3.15	0.03
0.90	3.63	0.05	4.51	0.06	6.01	0.06
1.00	4.64	0.06	7.57	0.05	10.42	0.03

[a] X_2 0.027. [b] X_2 0.021.

Here ΔH^0_{solv}, ΔH^0_{sol}, and ΔH^0_{vap} are the standard enthalpies (kJ mol^{-1}) of solvation, solution, and vaporization of the solute, respectively.

The plots of the solvation enthalpies of the alcohols vs. the composition of water–acetone mixtures are given in Fig. 1. It is seen that the solvation enthalpies increase with increasing number of hydroxy groups in the alcohols over the entire range of compositions of the mixed solvent. Similar results were obtained in [6] for water–methanol and in [9] for water–dioxane solvents. The main reason for such results is the ability of polyhydric alcohols to form several hydrogen bonds with the solvent. The trend in the solvation enthalpies of the series of hydrocarbons in the water–acetone solvent [10, 11] points to the fact that increasing size of the hydrocarbon radical, too, favors enhanced solvation of the compounds.

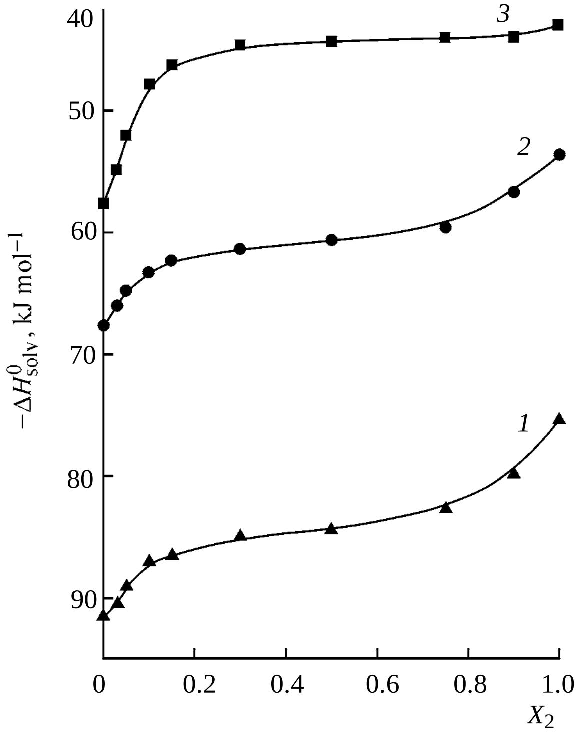

Fig. 1. Plot of the solvation enthalpies of (*1*) 1,2,3-propanetriol, (*2*) 1,2-ethanediol, and (*3*) 1-propanol in water–acetone mixtures vs. solvent compositions at 298.15 K (X_2 is the mole fraction of acetone).

With the aim to elucidate the effect of the composition of the solvent mixture on the solvation enthalpies of the alcohols we calculated the enthalpies of transfer of the latter from water to its mixtures with acetone (ΔH^0_{tr}) by Eq. (2).

$$\Delta H^0_{tr} = \Delta H^0_{sol} - \Delta H^0_{sol1}. \qquad (2)$$

Here ΔH^0_{sol} and ΔH^0_{sol1} are the enthalpies of solution of the alcohol in the mixed solvent and in water, respectively.

The concentration dependences are given in Fig. 2. Three characteristic portions can be recognized in the isotherms of the transfer enthalpies. In the region of small additions of the nonaqueous component (the mole fraction of the nonaqueous component in a mixed solvent X_2 ~0–0.3), the endothermicity of alcohol transfer sharply increases. In the medium composition range (X_2 ~0.3–0.7), the transfer enthalpies scarcely change, and then, at $X_2 > 0.7$, the ΔH^0_{tr} values increase again.

Comparison of the dependences given in Figs. 1 and 2 shows that the structure and properties of the solute have an essential impact on the solvation enthalpies (Fig. 1) and much weaker affect the transfer enthalpies (Fig. 2). The composition of the mixed solvent exert a qualitatively similar effect on the ΔH^0_{tr} of the alkanol, diol, and triol. However, in the water-rich region, the transfer enthalpies of PrOH change almost twice as much as the transfer enthalpies of $(CH_2OH)_2$ and $C_3H_5(OH)_3$. Taking into account that PrOH contains the minimal number of hydroxy groups among the alcohols studied, this change in ΔH^0_{tr} seems to be associated with decreasing energy of nonspecific solvation.

As the composition of the mixed solvent is varied, a compensation is observed of changes in nonspecific and specific solvation of mono- di-, and trihydric alcohols in whose molecules each carbon atom bears one hydroxy group. In Fig. 2, 1,2-ethanediol and 1,2,3-propanetriol belong to such alcohols. Similar

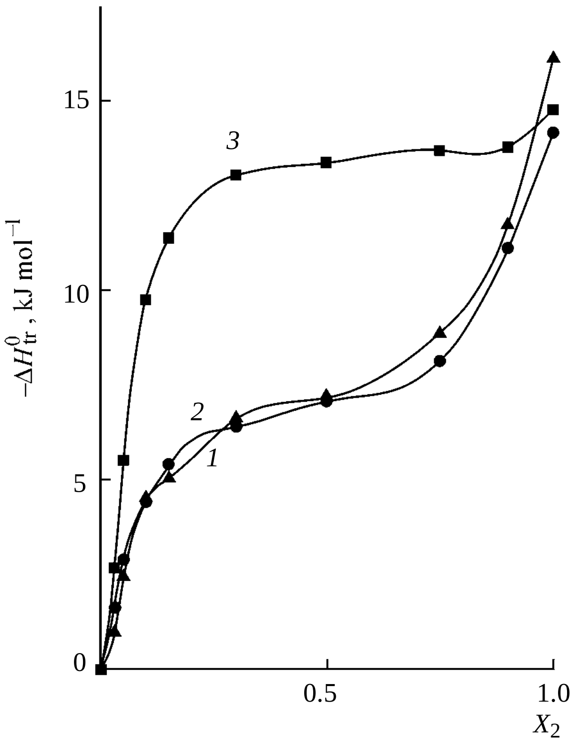

Fig. 2. Plots of the transfer enthalpies of (*1*) 1,2,3-propanetriol, (*2*) 1,2-ethanediol, and (*3*) 1-propanol from water to its mixtures with acetone vs. solvent compositions at 298.15 K (X_2 is the mole fraction of acetone).

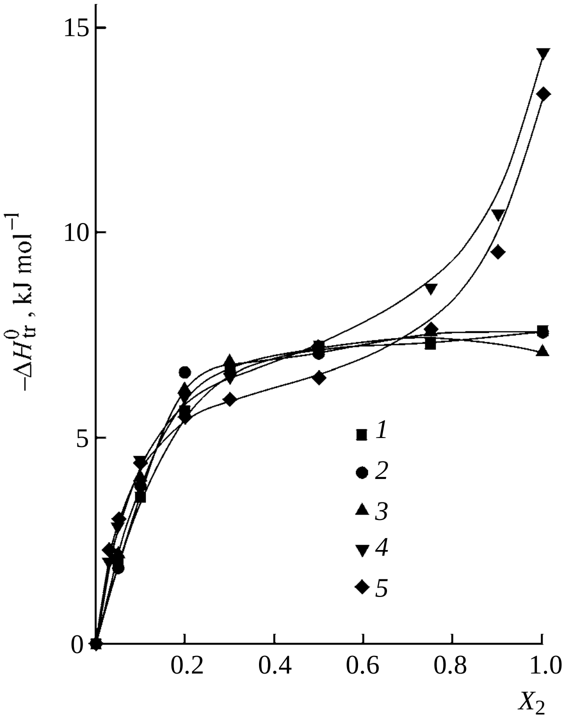

Fig. 3. Plots of the transfer enthalpies of (*1*) methanol, (*2, 4*) 1,2-ethanediol, and (*3, 5*) 1,2,3-propanetriol from water to its mixture with (*1, 3*) methanol and (*4, 5*) 1,4-dioxane (X_2 is the mole fraction of methanol).

effects are observed for MeOH, $(CH_2OH)_2$, and $C_3H_5(OH)_3$ in water–methanol mixtures and for $(CH_2OH)_2$ and $C_3H_5(OH)_3$ in water–1,4-dioxane mixtures (Fig. 3). The concentration dependences of ΔH^0_{tr} for the compounds given in Fig. 3 are plotted using data in [6, 9, 12].

It is evident that the transfer enthalpies of compounds in which each methyl, methylene, or methine radical bears one hydroxy group are approximately the same over the entire range of mixture compositions. Note that a similar phenomenon is also observed with the enthalpies of transfer of the third component from water into its mixtures with MeOH, $(CH_2OH)_2$, and $C_3H_5(OH)_3$. In this case, alcohols act as co-solvents in mixtures with water. As an example we give in Fig. 4 the concentration dependences of ΔH^0_{tr} for hexamethylphosphoramide [13]. The reasons for such a compensation of changes in nonspecific and specific solvation of compounds are not yet understood. Nevertheless, the discovered regularities can be used to predict the transfer enthalpies of compounds. For example, the transfer enthalpies of MeOH, $(CH_2OH)_2$, and $C_3H_5(OH)_3$ from water into various mixed solvents can be determined, if ΔH^0_{tr} for one of them is known. The same can be done for the transfer enthalpies of nonelectrolytes from water to its mixtures with MeOH, $(CH_2OH)_2$, and $C_3H_5(OH)_3$, if data for one mixture are known. We can also state with assurance that such compensation effects in solvation in mixed solvents will be typical of higher alcohols in which the number of hydroxy groups is equal to the number of hydrocarbon fragments.

EXPERIMENTAL

Chemical grade 1-propanol and acetone were purified by conventional procedures [14]. Chemical grade ethylene glycol and glycerol were twice distilled in a vacuum at 353 and 360 K, respectively. The water contents of organic solvents were determined by Fischer titration [15] and did not exceed 0.03 wt%.

Mixed solvents were prepared by the gravimetric technique with an accuracy of 0.001 mole fraction using freshly twice distilled water (specific electrical conductivity 10^{-5} S/cm).

The solution enthalpies were measured in a variable-temperature isothermal-shell calorimeter. Its

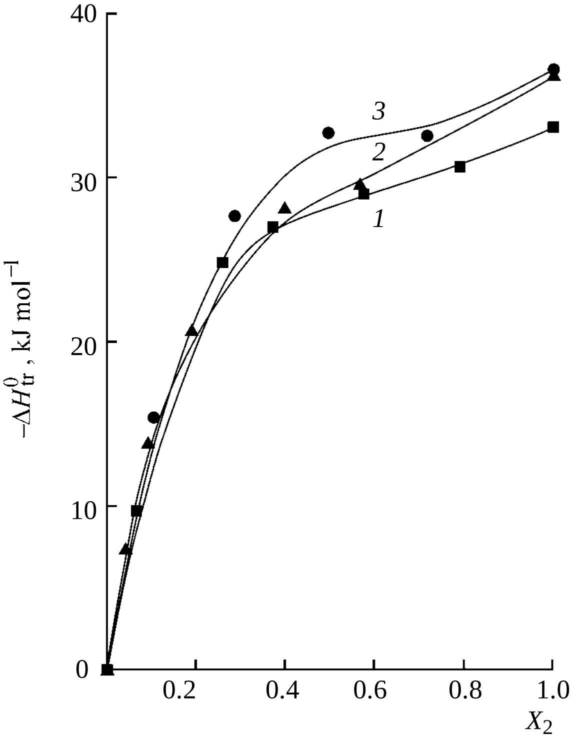

Fig. 4. Plots of the transfer enthalpies of hexamethylphosphoramide from water to its mixture with (*1*) methanol, (*2*) 1,2,3-propanetriol, and (*3*) 1,2-ethanediol (X_2 is the mole fraction of nonaqueous component).

design is similar to that described in [16]. The arithmetic mean heat effects of solution (ΔH^0_{sol}) were taken as standard solution enthalpies, since the differences between ΔH^0_{sol} values at varied alcohol concentrations did not exceed the experimental error.

REFERENCES

1. Rochester, C.H. and Wilson, D.N., *J. Chem. Soc., Faraday Trans. 1,* 1977, vol. 73, no. 4, p. 569.
2. Rochester, C.H. and Sclosa, S.A., *J. Chem. Soc., Faraday Trans. 1,* 1981, vol. 77, no. 3, p. 575.
3. Sharnin, V.A., *Doctoral (Chem.) Dissertation,* Ivanovo, 1996.
4. Cabani, S. and Gianni, P., *J. Chem. Soc., Faraday Trans. 1,* 1979, vol. 75, no. 5, p. 1184.
5. Cabani, S., Gianni, P., Mollica, V., and Lepori, L., *J. Solution Chem.,* 1981, vol. 10, no. 8, p. 563.
6. Egorova, N.G., Antonova, O.A., Batov, D.V., and Korolev, V.P., *Zh. Obshch. Khim.,* 1996, vol. 66, no. 2, p. 214.
7. Batov, D.V. and Korolev, V.P., *Izv. Ross. Akad. Nauk, Ser. Khim.,* 1997, no. 10, p. 1811.
8. Marcus, Y., *Ion Solvation,* New York: Wiley, 1985.
9. Kulikov, M.V. and Trutneva, E.Yu., *Izv. Ross. Akad. Nauk, Ser. Khim.,* 1997, no. 9, p. 1592.
10. Kulikov, M.V., Kropotova, M.Yu., and Korolev, V.P., *Zh. Obshch. Khim.,* 1996, vol. 66, no. 9, p. 1424.
11. Kulikov, M.V., Kropotova, M.Yu., and Korolev, V.P., *Zh. Obshch. Khim.,* 1997, vol. 67, no. 12 p. 1953.
12. Batov, D.V., Zaichikov, A.M., Slyusar, V.P., and Korolev, V.P., *Zh. Obshch. Khim.,* 1999, vol. 69, no. 12, p. 1953.
13. Krestov, G.A., Korolyov, V.P., and Batov, D.V., *Thermochim. Acta,* 1990, vol. 169, p. 69.
14. Gordon, A.J. and Ford, R.A., *The Chemist's Companion,* New York: Wiley, 1972.
15. Klimova, V.A., *Osnovnye mikrometody analiza organicheskikh soedinenii* (Basic Methods of Organic Microanalysis), Moscow: Khimiya, 1967.
16. Batov, D.V., Vandyshev, V.N., Korolev, V.P., and Krestov, G.A., *Zh. Fiz. Khim.,* 1983, vol. 57, no. 2, p. 253.