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Thermodynamic Characteristics of Solution of Polar Nonelectrolytes in Magnetized Water

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Abstract—The solution enthalpies of ten polar nonelectrolytes in water preliminarily exposed to a weak magnetic field were measured and compared with thermodynamic data for water and heavy water. The observed regularities provide evidence showing that magnetization affects physicochemical properties of water.

The wide application of water in industry necessitates search for intensifying processes involving water as the major component. Exposure of water and its solutions to electromagnetic field proved effective in textile dyeing. At the same time, the practical use of magnetized solutions and compositions goes ahead of development of the theory of magnetic treatment of liquids.

Literature analysis showed that there has been no commonly accepted mechanistic views on the effect of magnetic fields on water and its solutions [1]. We consider the most acceptable the "admixture" model of water magnetization. In terms of this theory, magnetization occurs due to the presence in the solvent of microparticles, ions, or microscopic air blebs [2]. Experimentally, the effect of magnetization shows up in various macroproperties of water (density, electrical conductivity, solubility of salts, etc.). However, this phenomenon has not been explained on a microscopic level. Sokol'skii [2] have explained changed thermodynamic properties of magnetized water by changes in hydration of dissolved admixtures. We considered it interesting to study the energetic characteristics of solvation of different compounds in magnetized water. The most reliable are calorimetric data. The published results [4, 5] show that the effects of magnetic fields on aqueous systems be can measured by the heats of solution of electrolytes possessing marked hydrophilic and hydrophobic properties. As demonstrated in [5], such measurements are appropriate to perform in an equilibrium thermodynamics apparatus, since relaxation of solution properties occurs not immediately after magnetic treatment but within 60–90 min. Evidence for this conclusion comes from specific electrical conductivity measurements and thermochemical experiments with potassium chloride 30–40 min after magnetic treatment. Note that the conditions of magnetic treatment and calorimetry are similar to those described in [5], with one essential exception that we used a polar nonelectrolyte "probe" (AB), which seems more fruitful in terms of both calorimetric experiment (better solution kinetics) and data treatment.

According to the present notion of the thermodynamics of solvation of polar molecules [6 ,7], the enthalpy of transfer is a sum of universal and specific components. To assess the role of the universal component, one is convenient to consider a series of lower aliphatic alcohols which have close donor (*DN*) and acceptor numbers (*AN*) and dipole moments (μ) and much different molar volumes (V_m) (Table 1). As seen from the resulting data, the exothermicity of solution in magnetized water decreases along the alcohol series compared with the initial distillate. Therewith, the endothemicity of the enthalpy of transfer increases with increasing hydrocarbon chain length in the alcohol molecule. From the linear dependence we estimated the increment for the enthalpy of transfer $\Delta H^0_{tr}(CH_2)$ at 74 J/mol. A feature of water as a solvent strongly associated by hydrogen bonding is that the more disordered its structure the harder is solute to form a cavity and take place in it [6]. In this connection one may suppose that the enhanced endo effect of alcohol transfer from H_2O into its magnetized analog H_2O^* is explained by disordering the water structure under magnetic treatment. Thus, the nonspecific (universal) [7] component of the enthalpy of transfer from H_2O to H_2O^* increases along the alcohol series studied, on account of increased endothermic contribution from cavity formation in H_2O^* compared with H_2O.

As shown in [8], magnetic susceptibility data for aqueous solutions of electrolytes are useful to compare with data for heavy water. We found linear dependences between the magnetization effect and the

Table 1. Magnetization effect from the enthalpies of transfer of aliphatic alcohols (298.15 K)

Alcohol	Properties of solute				Enthalpy of transfer $\Delta H^0_{H_2O \to H_2O^*}(AB) \pm S_f$, J/mol
	DN, kcal/mol	*AN*, kcal/mol	V_m, cm^3/mol	μ, D	
MeOH	19.0	41.3	40.9	1.70	58±53
EtOH	18.5	37.1	58.7	1.69	132±60
PrOH	18.0	33.5	75.2	1.66	210±30
BuOH	19.5	26.3	92.0	1.61	280±86

Table 2. Magnetization effect from the enthalpies of solution of polar nonelectrolytes (298.15 K)[a]

Comp. no.	Properties of solute				Enthalpy of transfer $\Delta H^0_{H_2O \to H_2O^*}(AB) \pm S_f$, J/mol
	DN, kcal/mol	*AN*, kcal/mol	V_m, cm^3/mol	μ, D	
I	38.8	10.6	175.7	5.40	983±71
II	26.6	16.6	77.4	3.80	380±40
III	29.8	19.3	71.3	4.00	380±120
IV	19.2	–	11.2	3.90	10±70
V	24.0	39.8	39.9	–	0±40
VI	14.1	18.9	52.9	3.73	–170±50
VII	2.7	29.5	54.0	3.20	–130±40

[a] HMPA (**I**), DMF (**II**), DMSO (**III**), diethylformamide (**IV**), formamide (**V**), acetonitrile (**VI**), and nitromethane (**VII**).

isotope effect [$\Delta H^0_{D_2O \to H_2O}(AB)$] calculated from the thermochemical data for solutions of polar nonelectrolytes AB (aliphatic alcohols inclusive), obtained in [7] (Fig. 1, plot *2*). Drawing an analogy between the enthalpy characteristics of hydration of the compounds in hand in H_2O^*, D_2O, and H_2O, we can suggest the following.

According to [9], D_2O is a stronger structured liquid than H_2O due to stronger hydrogen bonds. The isotope difference in the H-bond energies is estimated at ~1.4 kJ/mol [9]. The observation of linear correlations (Fig. 1) may suggest destructuring of water under magnetic treatment, which is consistent with the speculations of Mokrousov and Gorlenko [8] that magnetic field favors destruction of hydration environment of solutes. The effect of magnetic treatment of water here is associated with "changes in the structural organization of the physicochemical system, involving primarily formation of new water associates".

Let us now consider how magnetization affects universal interactions in distilled water. Taking into account that the molecular polarizability of D_2O is lower than that of H_2O (1.45277 and 1.46458 D [9], respectively), we can consider natural that the energy of dispersion interactions in D_2O is lower than in water.

The observed correlations with isotope effects show that the energy of universal (dispersion) interactions of polar molecules in H_2O^* is higher than in H_2O. This relates exclusively to dispersion interactions, provided mutual compensation of inductive and orientational interactions on solvation of polar molecules in H-bonded solvents is assumed [10].

Thus, the increasing endothermicity of the $H_2O \to H_2O^*$ transfer along the alcohol series can be explained in terms of decreased contribution of nonspecific solvation, associated with the prevalence of the contribution of void formation over the contribution of universal interactions. It should be noted that the above conclusion as to the trends in variation of the universal contribution into the hydration enthalpy of alcohols in magnetized water is also valid for the polar nonelectrolytes presented in Table 2. A fair correlation with the isotope effect was obtained (Fig. 1, plot *2*).

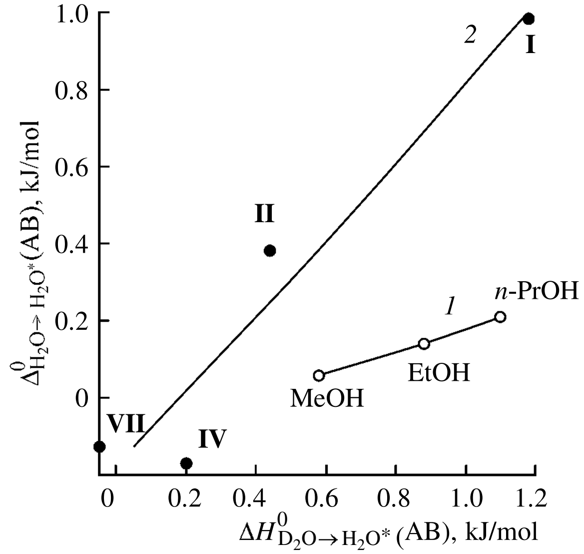

Fig. 1. Dependences of magnetization of (*1*) alcohols and (*2*) nonassociated nonelectrolytes (Table 2) on the enthalpies of transfer of these nonelectrolytes from heavy water to water.

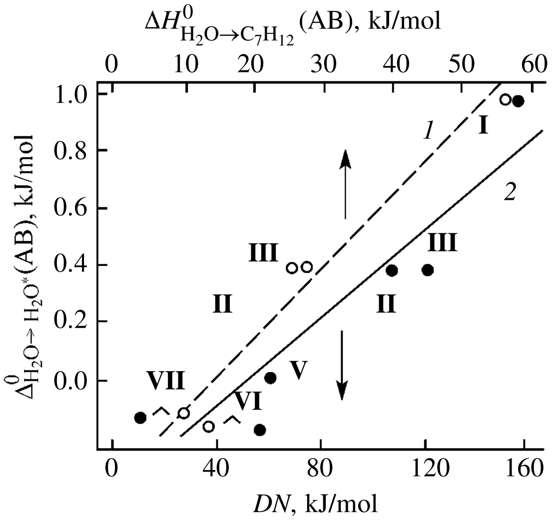

Fig. 2. Dependences of the enthalpies of transfer of nonelectrolytes (Table 2) from water to magnetized water (*1*) on the enthalpies of transfer of these nonelectrolytes from water into heptane and (*2*) on their donor numbers.

Figure 2 (plot *1*) shows the linear dependence of the magnetization effect on the enthalpy of transfer of five polar nonelectrolytes from water into heptane [$\Delta H^0_{H_2O\to C_7H_{16}}$(AB)]. The latter solvent has no H bonds and can be considered an unstructured liquid. Despite the fact that the isotope effects and the enthalpies of transfer of nonelectrolytes from water into heptane have different absolute values (Fig. 1, plot *2*), they both are linearly related to the magnetization effect. This result provides evidence for the conclusion that H_2O^* is weaker structured compared with H_2O.

Changes in H_2O^* structuring can induce formation of new forms of $H_2O\cdots H_2O$ associates and change the chemical activity of water (its molecules or constituent atoms). To check this assumption, we extended the range of solutes by nonelectrolytes with different parameters of chemical activity (*DN*, *AN*) with the aim to assess the contribution of specific (chemical) solvation into the $\Delta H^0_{H_2O\to H_2O^*}$(AB) values of polar molecules. As seen from Table 2, the enthalpies of transfer of amides from distillate to its magnetized analog span the range 0.0–973 J/mol and are slightly lower for acetonitrile and nitromethane.

Korolev *et al.* [11] have studied a wide range of polar nonelectrolytes to show that their hydration is largely dependent on donor–acceptor interactions. Since the H bonding between solute and water (proton donor) most frequently involves hydrogen atoms of the latter, the decrease in the exothermicity of hydration of polar molecules in magnetized water with increasing electron-donor capacity (nitromethane < formamide < DMF = DMSO < HMPT) may result from the fact that the electron-acceptor capacity (*AN*) of water is decreased by magnetization. Evidence for the above conclusion comes from the observation of a linear dependence between magnetization effect and donor number for certain nonelectrolytes (Fig. 2, plot *2*). Therewith, the strongest weakening of hydration on transfer from H_2O to H_2O^*, characteristic of HMPA (predominantly electron donor), can be related to the strongest decrease in the chemical component of the hydration enthalpy of this nonelectrolyte compared with the other compounds.

With the enthalpies of solution of HMPA in heptane and 8 polar solvents (water, nitromethane, DMSO, DMF, acetonitrile, formamide, diethylformamide, propylene carbonate) we obtained the following empirical equation.

$$\Delta H^0_{C_7H_{16}\to S}(\text{HMPA}) = 8.444 - 1.299AN;$$

$$n\ 8,\ r\ 0.964,\ S_f\ 0.125.$$

Here *AN* is the acceptor number of nonelectrolyte (Table 2) and S_f is the fitting error, kJ/mol.

Using this equation, from the $\Delta H^0_{H_2O\to H_2O^*}$ value for HPMT (983 J/mol), one can easily estimate the decrease in the electronacceptor capacity of magnetized water compared with nonmagnetized.

Below we give the resulting multiparameter equation relating experimental thermochemical data for nonassociated nonelectrolytes (Table 2) to physicochemical characteristics of the latter (except for formamide).

$$\Delta H^0_{H_2O\to H_2O^*}(\text{AB}) = 0.240 + 0.805DN - 0.669AN$$
$$+ 0.237V_m;\ n\ 6,\ r\ 0.989,\ S_f\ 0.190.$$

The equation shows that the enthalpy of $H_2O \to H_2O^*$ transfer is more contributed by donor-acceptor properties of solutes and less by their size. The positive signs of the second and fourth terms of the equation provide evidence for the above suggestion as to decreased structuring and electron-acceptor power of magnetized water. The negative sing of the third term of the equation shows that the exothermicity of solution in magnetized water decreases with decreasing electron-acceptor capacity of the "probe" molecule and points to increased electron-donor power of the latter.

Thus, the revealed regularities suggest that exposure to nonuniform magnetic field renders water less structured and, as result, weakens its electron-acceptor and enhances electron-donor properties.

EXPERIMENTAL

The purity of water used in calorimetric measurements was controlled by the electrical conductivity. Distillate with a specific electrical conductivity of $2.5 \times 10^{-5}\ \Omega^{-1}$/cm was taken for experiments. The heat effects of solution of aliphatic alcohols and certain polar nonelectrolytes in magnetized distillate at 298.15 K, we measured earlier, have been discussed in [12, 13]. The measurements were performed in an isothermic microcalorimeter [14] with an error of 0.6%. The heat equilibrium in the calorimeter was attained within 30 min after charging.

Magnetization was performed in a laboratory device made of an electromagnet with a glass pipe coiled on it perpendicularly to force lines. Distillate was passed at a rate of 0.3 m/s through the pipe. The static voltage was 160 kA/m. The magnetization effect $[\Delta H^0_{H_2O \to H_2O^*}(AB)]$ was calculated as a difference between the net heat effects of solution in the magnetized (H_2O^*) and initial distillate. The net heat effect was calculated as an arithmetic mean of 8–10 measurements in a narrow range of solute concentrations.

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