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Hydration of Non-electrolytes in H_2O and D_2O Investigated by Passynski's Method

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Abstract Passynski's hydration numbers were calculated for 1-propanol, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2,6-dimethylpyridine, and 2,4, 6-trimethylpyridine in H_2O and D_2O, for the temperature range from 277 K to 313 K. Correlations between the hydration numbers and the association energies of 1:1 water–amine complexes as well as the net atomic charges on the nitrogen atom were found. It seems probable that the O–H· · · N bond promotes the structure due to the strengthening of the O–H· · · O bonds between water molecules neighboring that of amine. The higher the O–H· · · N bond energy, the stronger is the promoting effect. The calculated hydration numbers in H_2O are lower than their counterparts in D_2O. Thus D_2O appears more sensitive than H_2O to the solute-induced changes of structure.

Keywords Aqueous solutions · Compressibility · Hydrogen bond · Pyridines

1 Introduction

The hydration number is usually understood as the number of water molecules around an ion, whose properties are different from those in the bulk phase [1]. In extended meaning, the term applies to non-electrolytes as well. Different physicochemical properties may be applied in calculations of the hydration numbers. Passynski suggested a method that takes into account changes in compressibility on addition of a solute to solvent water [2,3]. The calculations are based on the assumption that the solute molecule and water in the hydration sphere are incompressible, while water outside that

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Paper dedicated to Prof. Dr. Stefan Ernst on the occasion of his 75th birthday.

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sphere remains unchanged in comparison to the pure bulk one. Thus, the compressibility of dilute binary aqueous solution is smaller than that of pure water. Passynski's considerations led to the following formula [2,3]:

$$n_\mathrm{h} = \left(1 - \kappa_S/\kappa_{S,1}{}^{\circ}\right) n_1/n_2, \tag{1}$$

where n_h was the hydration number, κ_S and $\kappa_{S,1}{}^{\circ}$ were the coefficients of isentropic compressibility of the solution and the pure solvent, respectively, and n_1/n_2 was the solvent-to-solute molar ratio in the mixture.

Very recently, Burakowski and Gliński [4–7] thoroughly studied the hydration of alcohols, ketones, carboxylic acids, amines, and amino-acids using Passynski's method. They found that Passynski's hydration numbers are group additive quantities that strongly supported the idea about physical meaning of those numbers. The studies [4–7], although extensive, dealt with the temperature 298.15 K and the light water solvent (H_2O). That tempted us to calculate the hydration numbers of several non-electrolytes in heavy water (D_2O). Moreover, we traced the influence of temperature on the hydration numbers in the two solvents, H_2O and D_2O. The isotopic exchange in water solvent may dramatically influence properties of aqueous systems, e.g., cause the phase separation [8]. That is also manifested in thermodynamic functions. In another paper devoted to binary mixtures containing H_2O and D_2O, we have shown that the excess internal pressure is particularly sensitive to the isotopic composition of water [9]. Unfortunately, the internal pressure cannot be measured in a direct way, but it is rather calculated using combined data obtained by various experimental methods, e.g., acoustical, densimetric, and calorimetric. Passynski's approach requires just the speeds of sound and densities of the mixtures that makes the experimental procedure and calculations simpler.

2 Calculations

Passynski's hydration numbers were calculated for 10 systems at atmospheric pressure, in the temperature range from 277 K to 313 K. The systems were dilute binary solutions of 1-propanol, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2,6-dimethylpyridine, and 2,4,6-trimethylpyridine in light water (H_2O) and 1-propanol, 2-methylpyridine, 3-methylpyridine, and 4-methylpyridine in heavy water (D_2O). Maximum mole fractions of solutes did not exceed 0.05. The experimental data indispensable in calculations, i.e., the densities (ρ) and speeds of sound (u), were obtained in our laboratory [10–18], except those for 1-propanol + H_2O that were taken from the literature [19].

In the ultrasonic measurements [10–18], two techniques were applied: the pulse-echo-overlap and the sing-around method. The ultrasonic cells are built of stainless steel as vertical cylinders of 30 mm or 50 mm in diameter, with two piezoceramic transducers mounted opposite to one another on the side wall. The wave frequencies are 2.7 MHz in the pulse-echo-overlap apparatus and 4 MHz in the sing-around one. Densities were measured using bicapillary pycnometers or vibrating-tube densimeter. Experimental details are reported in previous works [10–18].

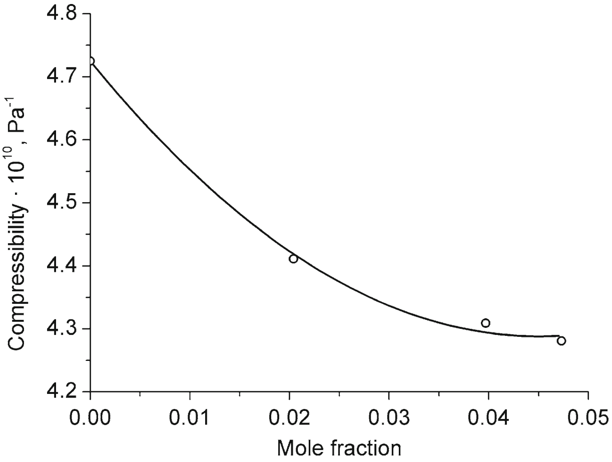

Fig. 1 Isentropic compressibility of 4-methylpyridine in D_2O as a function of mole fraction of the solute at 20 °C. Points (○) calculated from data reported in [10], line: second-order polynomial interpolation, Eq. 3

The isentropic compressibilities were calculated from Laplace's formula:

$$\kappa_S = \rho^{-1} u^{-2}. \tag{2}$$

The dependencies of compressibility on the mole fraction of solute (x_2) were satisfactorily approximated by the second-order polynomials:

$$\kappa_S = \kappa_{S,1}{}^{\circ} + a x_2 + b x_2^2, \tag{3}$$

where $\kappa_{S,1}{}^{\circ}$ is the compressibility of pure solvent (H_2O or D_2O), and a and b are regression coefficients obtained by the least squares method. Illustration of the quality of fit is given in Fig. 1. Substitution of the right-hand-side of Eq. 3 for κ_S, and x_1/x_2 for n_1/n_2 to Eq. 1 gives the following formula for the hydration number:

$$n_{\mathrm{h}} = -(1 - x_2)(a + b x_2)/\kappa_{S,1}{}^{\circ}. \tag{4}$$

It is evident that n_{h} calculated from Eq. 4 depends on concentration. That results from the solute–solute interactions in the mixture. To minimize this effect, the hydration numbers in infinitely dilute solutions were calculated:

$$n_{\mathrm{h}}^{\infty} = \lim_{x_2 \to 0} n_{\mathrm{h}} = -a/\kappa_{S,1}^{\circ}. \tag{5}$$

3 Results

The hydration number of 1-propanol in H_2O has been determined by Burakowski and Gliński [5–7] in very diluted solutions at 25 °C. For those mixtures, the dependencies of compressibility on the mole fraction were linear. Our method of calculations is based

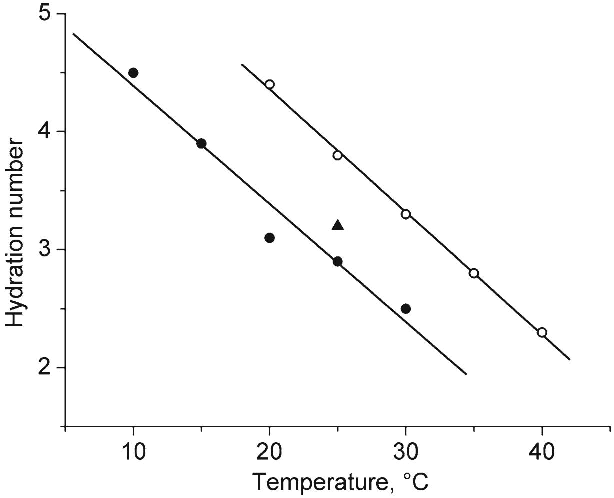

Fig. 2 The hydration numbers of 1-propanol in D_2O (○) and in H_2O (●) as functions of temperature, calculated from the data reported in [18] and [19], in comparison with the result for 1-propanol in H_2O at 25 °C (▲) reported by Burakowski and Gliński [4,6,7]

on data from a wider interval of concentrations. That required a parabolic function (Eq. 3) rather than the linear one. A comparison of our results for 1-propanol with that of Burakowski and Gliński [5–7], given in Fig. 2, evidences that both approaches lead to nearly the same results. Thus, we used the parabolic functions in the calculations of n_h^∞ for the eight systems containing methylpyridines. The hydration numbers for the methylpyridines in H_2O and D_2O are plotted versus temperature in Figs. 3 and 4. As could be expected, the n_h^∞ values decrease with increasing temperature.

4 Discussion and Conclusions

The hydration numbers depend on the size of solute molecules (Fig. 3)—trimethylpyridine molecules are larger than those of dimethylpyridine and of monomethylpyridines. As recently suggested—the hydration number is a group-additive quantity [6,7]. The group contribution approach proved to be particularly suitable for molecules with simple hydrocarbon chains, such as monohydroxyl alcohols, primary amines, and monocarboxylic acids. Our results point to semi-quantitative correlation between the hydration numbers and the molecular structure, similar to those for amino acids and diols [6]. The methylpyridines can be listed according to the increasing hydration numbers in the following way: 3-mpy ≤ 4-mpy < 2-mpy < 2,6-dmpy < 2,4,6-tmpy. The first three molecules are approximately of the same size; thus, the larger hydration number of 2-methylpyridine in comparison with those of 3- and 4-methylpyridine is most probably due to stronger O–H· · · N bonds. Plots of hydration numbers versus the association energy of 1:1 water–amine complexes and versus the net atomic charge on N (Figs. 5, 6) show remarkable correlation between these quantities.

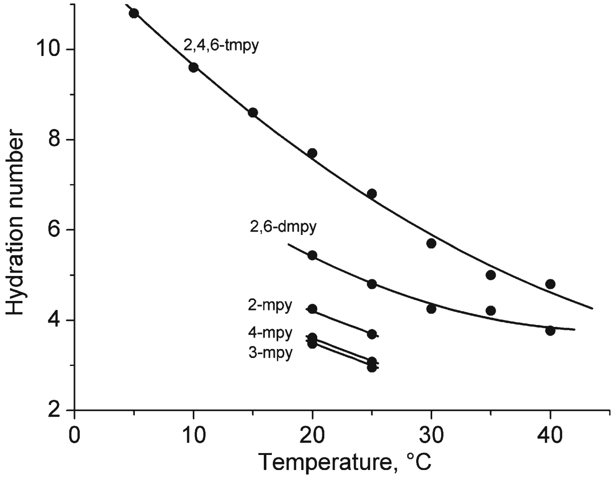

Fig. 3 The hydration numbers of methylpyridines in H_2O as functions of temperature, calculated from the data for 2-methylpyridine [11], 3-methylpyridine [12], 4-methylpyridine [13], 2,6-dimethylpyridine [14], and 2,4,6-trimethylpyridine [15]

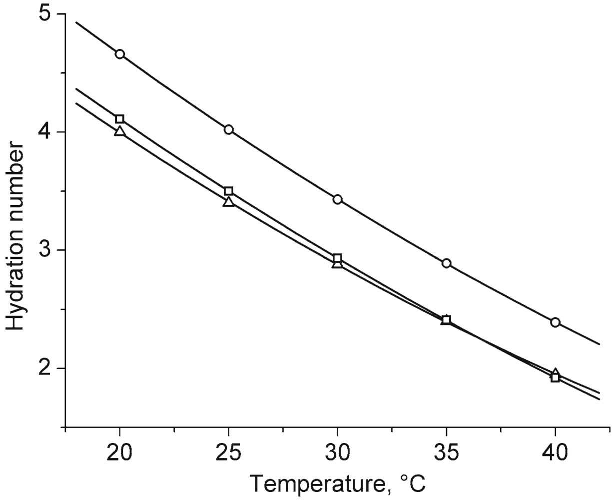

Fig. 4 The hydration numbers of 2-methylpyridine (○), 3-methylpyridine (Δ), 4-methylpyridine (☐) in D_2O, calculated from data reported in [16,17,10]

The hydration of methylpyridines seems to have mixed, hydrophobo–hydrophilic character. In previous works [11–13,15] we postulated clathrate-like structures in dilute aqueous solutions of methylpyridines. Due to the O–H· · · N bonds being stronger than the O–H· · · O ones (ca. $27\,\text{kJ}\cdot\text{mol}^{-1}$ vs. $20\,\text{kJ}\cdot\text{mol}^{-1}$) [22], the methylpyridine molecules undoubtedly form cross-associates with water. Since water itself is an associated liquid, the hydration structures seem to resemble those of semiclathrates. In the semiclathrates, the guest molecule is bonded to the host lattice. Thus the rotation of the guest in the host cage is limited in comparison with that in normal clathrates. That

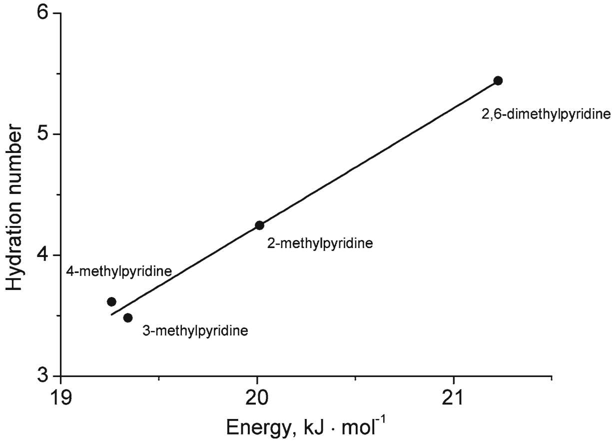

Fig. 5 Correlation of the hydration numbers of the pyridine derivatives determined at 20 °C with the association energies E of the 1:1 water–amine complexes reported in the literature [20]

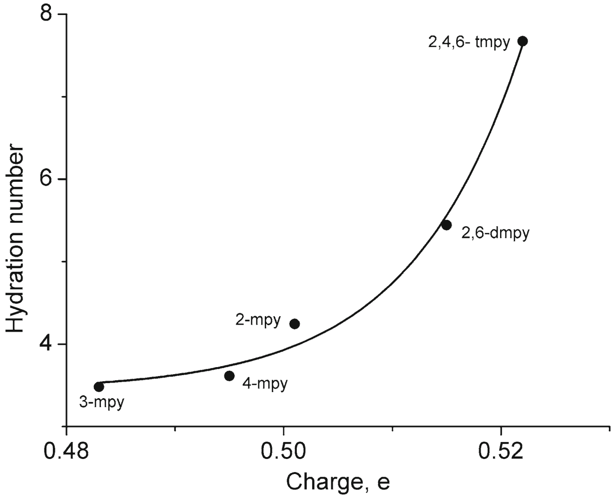

Fig. 6 Correlation of the hydration numbers of H_2O for the pyridine derivatives, determined at 20 °C, with the net atomic charges on the ring nitrogen atom (q/e) calculated theoretically [20,21]

makes the formation of semiclathrates less favorable than normal clathrates because of lower entropy. A relatively strong O–H· · · N bond formed between the methylpyridine and water shell compensates that effect, and the solvation is an enthalpy-driven process. Indeed, the liming enthalpies of solution of methylpyridines in water [23], as well as water in the methylpyridines [24] are negative and the dissolution is a highly exothermic process. The enthalpies follow the same sequence as the hydration numbers. However, the hydration numbers calculated from Eq. 5 are evidently too small for the number of water molecules in the host polyhedron formed around the relatively big solute molecule. It seems probable that the O–H· · · N bond promotes the structure

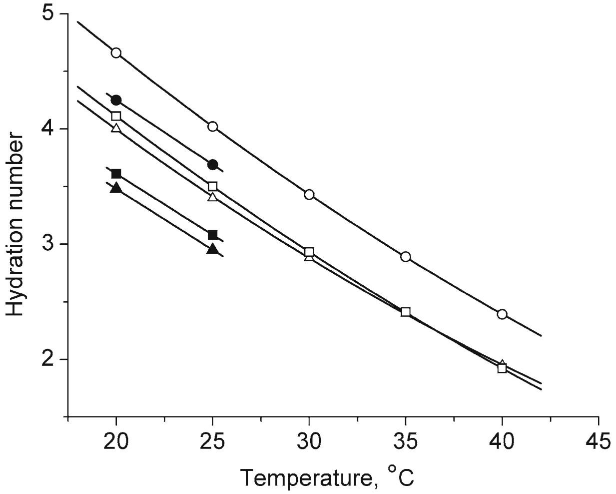

Fig. 7 Comparison of the hydration numbers of monomethylpyridines in H_2O (*filled symbols*) and in D_2O (*open symbols*) as functions of temperature; symbols as in Fig. 4

due to the strengthening of the O–H$\cdots$O bonds between water molecules neighboring that of amine. This co-operative promoting effect due to the nitrogen atom would gradually weaken for the more distant water molecules. Eventually, there would be no difference between water in the hydration sphere and that in the bulk phase.

All calculated hydration numbers decrease with increasing temperature (Figs. 2, 3, 4). The temperature dependencies of n_h^∞ are probably slightly concave functions rather than straight lines. That can be observed for the systems investigated in the wide temperature interval, especially 2,4,6-trimethylpyridine + H_2O, but also 2,6-dimethylpyridine + H_2O and the D_2O solutions. It seems to be a general rule, fulfilled also by the monomethylpyridines in H_2O, although the narrow range of temperature makes the concavity too small to be noticed. The $n_\mathrm{h}^\infty(t)$ functions for 1-propanol are steeper than those for methylpyridines. That indirectly confirms the idea of cooperativity presented above. The influence of the hydroxyl group of alcohol on the hydrogen-bonded network of water is weaker than that of the nitrogen atom—the difference between water–water and water–alcohol hydrogen bonds is small, and the co-operative structure-promoting effect could be less pronounced. Consequently, the hydration shell is less temperature-resistant than those around methylpyridine molecules.

The substitution of D_2O for H_2O influences the hydration numbers in a similar way as the decrease of temperature by ca. 3 °C to 5 °C for the methylpyridine solutions and by ca. 10 °C for those of 1-propanol (cf. Figs. 2 and 7). Thus, the hydration numbers in D_2O are significantly higher than their counterparts in H_2O. The stronger influence of the solute molecule on the structure of D_2O than H_2O is manifested in larger values of the coefficients a in Eq. 5 for the former systems. The difference in a coefficients for the two solvents is sufficient to compensate the effect of higher compressibility of D_2O; the isentropic compressibilities of D_2O and H_2O are $4.726 \times 10^{-10}\ \mathrm{Pa}^{-1}$ and $4.559 \times 10^{-10}\ \mathrm{Pa}^{-1}$ at $t = 20\,°\mathrm{C}$, respectively.

The discussion presented above showed that Passynski's approach might be an alternative to the thermodynamically strict analysis of compressibilities, e.g., in terms of partial functions, and compressibility-related functions, such as the internal pressure. In spite of rather arbitrary assumptions, the method leads to sound conclusions about the nature of the hydration phenomena. It is obvious an advantage is simplicity of the experiment as well as of the calculations.

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