

Sound Velocity, Density, and Compressibility in Solutions of Hexamethylphosphoric Triamide in H₂O and D₂O

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Sound velocity and density measurements for H₂O and D₂O solutions of hexamethylphosphoric triamide (HMPT), [(CH₃)₃N]₃PO at 25 °C have been carried out. The concentration dependence of the molar volumes and adiabatic compressibilities calculated therefrom are interpreted in terms of the water structure. The differences found between the H₂O and D₂O solutions are similarly explained.

Aqueous HMPT solutions are of interest in the study of hydrophobic interactions and structural variations of water. Recently, the large retarding action of HMPT on the rotational mobility of water molecules¹⁾ has been observed. HMPT is miscible in all proportions with water, forming strong hydrogen bonds.²⁾ Having several nonpolar groups, HMPT can be regarded as a simplified model element of biopolymers that exhibit complex interactions with water. With this in mind, we have conducted a study of sound velocity, density and compressibility of HMPT solutions in H₂O and D₂O to elucidate the characteristics of the hydration of this molecule.

Experimental

The sound velocity, U , in aqueous HMPT solutions over the concentration range used was determined by two methods. For both H₂O and D₂O solutions, a sing-around ultrasonic velocimeter UVM-2 (Cho-onpa Kogyo) at 5 MHz was used. Deionized, distilled and deaerated water was used as a calibration liquid. The standard U values of water were taken from the work of Greenspan and Tschiegg.⁴⁾ The measurements were performed with an accuracy of ± 4 cm s⁻¹ for each sample. A conventional ultrasonic interferometer method⁴⁾ at a frequency of 3 MHz was also used for H₂O solutions for comparison purposes. The accuracy of the measurements was within $\pm 0.2\%$.

The density of the aqueous HMPT solutions was determined at 25.00 °C with a digital precision densimeter, DMA 02C (Anton Paar). The instrument was placed in an air thermostat controlled at 25 ± 0.1 °C and the temperature of the sample solution was regulated by circulating water at a rate, *ca.* 6 dm³ min⁻¹ from an external thermostat with a stability of ± 0.001 °C. Reproducibility of the frequency for water was within $\pm 5 \times 10^{-7}$. The calibration was made with distilled mercury (Merck, Suprapur 13.5336 g cm⁻³),⁵⁾ water (0.997045 g cm⁻³)⁶⁾ and distilled toluene (Eastman Kodak, Spectrograde), the density of which was determined as 0.862247 g cm⁻³.^{7,8)} Calibration was repeated every day using water and the toluene.

HMPT (Aldrich, $n_D^{20} = 1.4579$, $d_4^{20} = 1.03$ g cm⁻³, bp = 230 to 232 °C at 740 mmHg) was used as received. For the interferometric method, HMPT purified by the method given in Ref. 9 was used. D₂O had 99.75% deuterium content.

Results

The sound velocity (U) and the density (d) for HMPT solutions in H₂O and D₂O, and also for 0.5

TABLE 1. DENSITY AND SOUND VELOCITY OF HMPT SOLUTIONS OF H₂O AND D₂O AT 25 °C

Mol % HMPT	Density (g/cm ³)	Sound velocity (m/s)
0 (H ₂ O)	0.997045	1497.33
0.9766	1.004443	—
1.0	—	1560 ^{a)}
1.9444	1.011610	1609.86
2.0	—	1605 ^{a)}
2.9853	1.018662	1647.37
3.0	—	1640 ^{a)}
4.9926	1.029508	1681.77
5.0	—	1676 ^{a)}
9.8211	1.042575	1662.74
10	—	1654 ^{a)}
14.9534	1.046143	1611.97
15	—	1610 ^{a)}
20	—	1557 ^{a)}
30	—	1488 ^{a)}
50	—	1416 ^{a)}
80	—	1358 ^{a)}
100	1.019 ^{a)}	1332 ^{a)}
0 (D ₂ O)	1.10406	1400.13
0.2525	1.10359	—
0.5202	1.10330	1441.57
0.9925	1.10299	1473.03
1.1587	1.10288	1484.18
1.6111	1.10288	—
2.1899	1.10314	1540.55
2.2188	1.10310	1542.01
3.2491	1.10344	1580.74
5.5882	1.10294	1620.415
9.7847	1.09764	1612.02
16.0006	1.08628	1565.52
22.1777	1.07523	1523.42
28.6169	1.06525	1481.34
48.2903	1.04439	1401.495
100 (HMPT)	1.019 ^{a)}	1336.62
0 (0.5 mol NaCl / 55.5 mol D ₂ O)	1.12347	—
0.5202 (mol% HMPT)	1.12175	—
1.6111	1.12070	—
3.2491	1.11812	—
5.5882	1.11506	—

a) Determined by ultrasonic interferometer.

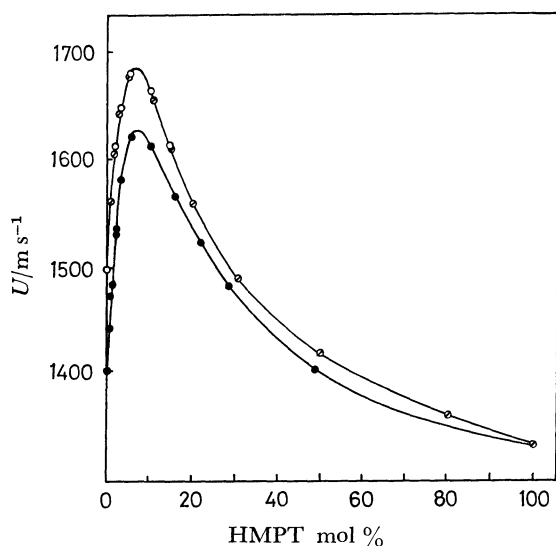


Fig. 1. Ultrasonic velocity in aqueous solutions of HMPT at 25 °C: in H₂O (○, ultrasonic interferometer method; ○, sing-around method) and in D₂O (●, sing-around method).

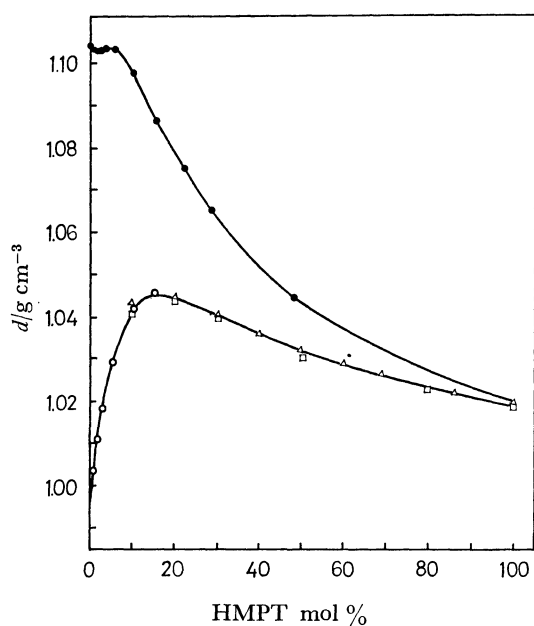


Fig. 2. Densities of aqueous solutions of HMPT in H₂O (○) and D₂O (●) at 25 °C. Data represented by △¹²⁾ and □²⁾ are taken from literatures.

mol dm⁻³ NaCl solution in D₂O at 25 °C are shown in Table 1. The value of the sound velocity for pure D₂O is consistent with reported values.^{10,11)} Figures 1 and 2 show the variations of U and d with HMPT concentration in H₂O and D₂O. In Fig. 2, the reported values^{2,12)} of the densities of HMPT solutions are also plotted. The sound velocity shows maxima at *ca.* 7 mol % HMPT in both H₂O and D₂O solutions.

The density of HMPT solutions in H₂O passes through a maximum at 15–20 mol % HMPT. On the other hand, the density of the solutions in D₂O shows a rather complicated variation with a minimum at 1.5% HMPT. The minimum in the D₂O solution disappears on addition of small amounts of NaCl.

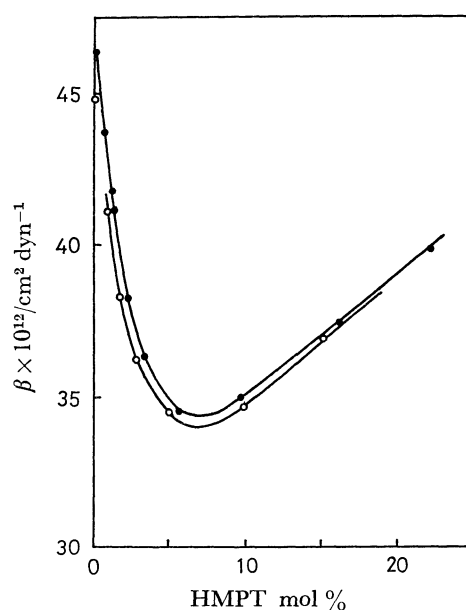


Fig. 3. Adiabatic compressibility of aqueous solutions of HMPT in H₂O (○) and D₂O (●) at 25 °C.

From the data of the sound velocity and the density for aqueous HMPT solutions, the adiabatic compressibility, β , was calculated. Figure 3 shows that β values for the H₂O and D₂O solutions pass minima at *ca.* 7 mol % HMPT. The variation of β is more pronounced in D₂O solutions than in H₂O solutions.

Discussion

The apparent molar volumes of HMPT calculated from the density data are presented in Fig. 4. A similar concentration dependence of apparent molar volumes is found for a number of hydrophobic molecules, *e.g.*, *t*-butanol, in aqueous solution.^{13–15)} The molecular mechanism of hydrophobic hydration can be described as a stabilization of water structure under action of nonpolar groups or molecules.^{19–22)} In the present case, the stabilization of water structure is ascribed to the filling of the cavities of the water structure with the nonpolar groups or molecules. As a consequence, the fraction of water molecules in the framework increases.^{16,18)} The concept of the inclusion of HMPT molecules in the cavities of water structure has been employed to explain some physicochemical properties of its aqueous solutions.^{1,2,22)} In terms of the structural model of nonelectrolytes in aqueous solution,^{17,23,24)} the volumetric changes on the introduction of HMPT molecules into water can be interpreted based on two effects; 1) the exclusion of free water molecules from the cavities caused by the occupation by HMPT molecules and the partial displacement of water molecules in the framework, and 2) the increase in the fraction of water molecules in the water tetrahedral structure outside the first coordination sphere of HMPT.

Given the similarity in the structures of light and heavy water^{25,26)} and the types of interaction between nonpolar groups of HMPT and H₂O and D₂O molecules in the cavities, there is a strong possibility that

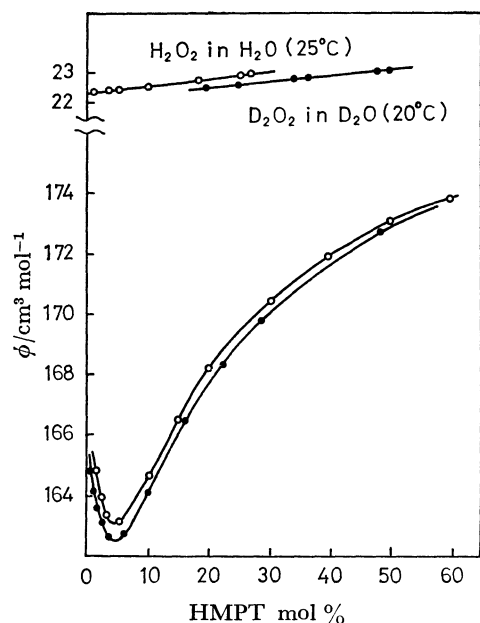


Fig. 4. Apparent molar volumes of HMPT at 25 °C and H_2O_2 ²⁷⁾ in H_2O (○) and D_2O (●).

HMPT has a similar effect on the structures of light and heavy water. However, as the fraction of the cavities filled with free water molecules in the D_2O structure is smaller than in the H_2O structure, the fraction of free water molecules excluded by HMPT molecules from the cavities, mainly into the framework, must be greater for H_2O solutions. Accordingly, the apparent molar volume of HMPT (ϕ_{HMPT}) in H_2O is expected to be greater than in D_2O , which is actually found in Fig. 4.

We can explain the concentration dependence of ϕ_{HMPT} in H_2O and D_2O solutions along the same lines. The first of the above mentioned volumetric effects, associated with the introduction of nonelectrolyte molecules into water in the concentration range where the solution structure is based on the tetrahedral water structure, is the same for solutions of polar or nonpolar molecules. This effect does not undergo any serious change in solutions where cavities are available. The second effect is not found for a nonelectrolyte that undergo hydrophilic hydration.^{23,24)} The concentration dependence of the apparent molar volume of H_2O_2 in aqueous solution,²⁸⁾ which is typical of a hydrophilic hydration, is shown in Fig. 4. The effect of increasing water structure outside the first hydration sphere around a hydrophobic molecule is such that, as the cavities become free of water molecules, each subsequent fraction of the molecule can eject from the cavities a smaller number of water molecules than the preceding one.

This process corresponds to a decrease in the apparent molar volume of HMPT with increasing concentration. It is expected to be observed up to the solution concentration corresponding to the complete or maximum possible filling of the water cavities with HMPT molecules. At higher concentrations, the durability of the water tetrahedral structure is exhausted and one can anticipate the initiation of transition to

a different type of the spatial ordering of the system with the appearance of the contacts, HMPT–HMPT and HMPT– H_2O –HMPT. At these concentrations, the filling of the cavity volume by HMPT molecules becomes less and less important. This is connected with the significant increase in the values of ϕ_{HMPT} beyond the concentration range corresponding to a water-like ordering. The same type of structural ordering found in light and heavy water warrants the same number of cavities in their structures and hence the occurrence of ϕ_{HMPT} minima at similar concentrations as actually observed in the experiments. The use of geometrical models to describe the introduction of HMPT molecules into the water structure with simultaneous substitution of the sites and cavity filling, enables one to estimate the concentration range where practically all water molecules bound to each other by a tetrahedral arrangement enter into the first surrounding sphere of HMPT molecules. At higher concentrations, the appearance of HMPT–HMPT contacts is observed by the X-ray method.²⁷⁾

The difference in the variations of the adiabatic compressibilities in H_2O and D_2O solutions (Fig. 3) can be explained using the same model for the solution structure. The sharper compressibility drop observed for D_2O solutions when changing from pure water to a solution is explained by a greater packing of D_2O structure when HMPT is added. This is due to the fact that the fraction of the cavities filled with water molecules is less for D_2O than for H_2O , and hence for D_2O , a smaller fraction of water molecules is excluded from the cavities into the sites on addition of HMPT. That the minimum values of β and of ϕ_{HMPT} in H_2O and D_2O solutions occur at approximately the same concentration follows from the similarity of the networks in H_2O and D_2O when all the molecules are located in the sites. The slight differences in the concentrations corresponding to the minimum ϕ_{HMPT} and β are likely to be related to the different structural states of the system at these concentrations. In the model under discussion, the first minimum corresponds to the maximum possible cavity filling when all the water molecules are distributed over the hydrate spheres, but a certain number of intermediate cavities may still exist. The minimum value of β can be related to a more complete cavity filling with simultaneous appearance of the contacts, HMPT–HMPT and HMPT– H_2O –HMPT.

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References

- 1) V. S. Goncharov, P. Ya. Yastremsky *et al.*, *Zh. Fiz. Khim.*, **54**, 789 (1977).
- 2) Yu. M. Kessler, V. P. Yemelin *et al.*, *Zh. Strukt. Khim.*, **16**, 797 (1977).
- 3) V. I. Stremousov, *Zh. Fiz. Khim.*, **36**, 380 (1962).
- 4) M. Greenspan and C. E. Tschiegg, *J. Res. Nat. Bureau*

Stand., **59**, 249 (1957).

5) "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," ed by E. W. Washburn, McGraw-Hill (1926), II, p. 457.

6) G. S. Kell, *J. Chem. Eng. Data*, **20**, 97 (1975).

7) "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum College Section, Texas (loose-leaf sheet dated October 31, 1950).

8) O. Kiyohara and G. S. Benson, *J. Chem. Thermodyn.*, **9**, 691 (1977).

9) Yu. M. Kessler, M. G. Fomichyova, N. M. Alpatova, and B. P. Yemelin, *Zh. Strukt. Khim.*, **13**, 517 (1972).

10) O. Kiyohara, C. J. Hapin, and G. S. Benson, *Can. J. Chem.*, **55**, 3544 (1977).

11) R. N. Gupta, P. C. Jain, and V. S. Nanda, *J. Chem. Thermodyn.*, **8**, 627 (1976).

12) Jean-Yves Gal and F. Persin, *C. R. Acad. Sci., Ser. C*, 282 (1976).

13) F. Franks, "Water—a Comprehensive Treatise," ed by F. Franks, Plenum Press, N. Y. (1975), Vol. IV.

14) F. Franks, *Ann. N. Y. Acad. Sci.*, **125**, 277 (1965).

15) C. deVisser, G. Perron, and J. E. Desnoyers, *J. Am. Chem. Soc.*, **99**, 5894 (1977).

16) P. S. Yastremsky, G. V. Kokovina, A. K. Lyashchenko, O. Ya. Samoilov, and Yu. A. Mirgorod, *Zh. Fiz. Khim.*,

49, 1442 (1975).

17) A. K. Lyashchenko, *J. Res. Inst. Catal., Hokkaido Univ.*, **25**, 129 (1978).

18) P. S. Yastremsky, G. V. Kokovina, A. K. Lyashchenko, and Yu. A. Mirgorod, *Zh. Strukt. Khim.*, **16**, 1002 (1975).

19) Z. I. Grigorovich and O. Ya. Samoilov, *Zh. Strukt. Khim.*, **3**, 404 (1962).

20) V. A. Mikhailov, *Zh. Strukt. Khim.*, **2**, 677 (1961).

21) G. G. Malenkov, *Zh. Strukt. Khim.*, **7**, 331 (1966).

22) O. Ya. Samoilov, P. S. Yastremsky, and V. S. Goncharov, *Zh. Strukt. Khim.*, **17**, 844 (1976).

23) A. K. Lyashchenko, V. S. Goncharov, and P. S. Yastremsky, *Zh. Strukt. Khim.*, **17**, 1020 (1976).

24) A. K. Lyashchenko and P. A. Stunjas, Preprints of the All-Union Conference on Calorimetry and Chemical Thermodynamics, Gvanovo, U.S.S.R., 1979.

25) I. B. Rabinovich, "The Effect of Isotope on the Physicochemical Properties of Liquids," ed by M. Nauka, 1968.

26) A. H. Harten and H. A. Levy, *Science*, **165**, 447 (1969).

27) V. I. Korsunsky and Yu. I. Naberukhin, *Zh. Strukt. Khim.*, **18**, 587 (1977).

28) P. A. Gigulze, O. Krop, and M. Falk, *Can. J. Chem.*, **36**, 883 (1958).