



# Temperature-dependent standard volumetric properties of hexamethylenetetramine in ordinary and deuterated water: A study resolving debatable issues being commented in the [Journal of Molecular Liquids, 248 (2017) 48–52]

Evgeniy V. Ivanov \*

Laboratory of Thermodynamics of Solutions of Nonelectrolytes and Biologically Active Substances, G.A. Krestov Institute of Solution Chemistry, Russian Academy of Sciences, 1 Akademicheskaya Str., 153045 Ivanovo, Russian Federation

## ARTICLE INFO

### Article history:

Received 2 August 2018

Received in revised form 6 September 2018

Accepted 9 September 2018

Available online 19 September 2018

### Keywords:

Hexamethylenetetramine

Standard volume and expansibility

Ordinary and heavy water

## ABSTRACT

In the above paper, I have debated the reliability of the existing literature data on the standard (partial at infinite dilution) molar volumes and expansibilities of hexamethylenetetramine (HMT) in heavy water ( $D_2O$ ) and the corresponding  $D_2O$ – $H_2O$  solvent isotope effects. Based mainly on the results of two works under comparison [C.M. Romero and H.J. Mesa, *J. Mol. Liq.* 242 (2017) 244–248; Yu.P. Pankratov and V.K. Abrosimov, *Russ. J. Phys. Chem.* 71 (1997) 1263–1266], a general conclusion about the pronounced inconsistencies in the discussed quantities for the solute in both in ( $H_2O + HMT$ ) and ( $D_2O + HMT$ ) has been made. This fact initiated a necessity carrying out the additional high-precision densimetric study of these binary liquid systems, followed by estimating the volume-isotope characteristics of interest. Such a study has been done and its results are reported in the present work. Primarily, it is confirmed here the conclusion on the doubtfulness of results derived by both authors' groups being analyzed in comparison.

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## 1. Introduction

In a recent paper appearing in this *Journal* [1], I have carried out the comparative analysis of some thermodynamic quantities reported in two experimental works, by Romero & Mesa [2] and Pankratov & Abrosimov [3], for the same binary aqueous systems. The case in point is the temperature-dependent values of standard (partial at infinite dilution) molar volume,  $V_m^0$ , and isobaric expansibility,  $E_p$ , of hexamethylenetetramine (hereinafter, HMT) being the well-known *urotropine* or *hexamine* pharmaceutical in water H/D isotopologues ( $H_2O$  and  $D_2O$ ). Two main points relating to the problem were considered in my comments [1]. Namely, how are plausible the volumetric characteristics being compared [2,3] and how they are correlated with the predicted nature of the HMT hydration?

If one carefully reads the papers [2,3] one discovers that a rather ambiguous situation is observed at comparing the data on  $V_m^0$  and  $E_p$  for the system ( $D_2O + HMT$ ). So, the former quantities differ catastrophically between themselves (by ca.  $11 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ , on an average!). In turn, given the fact that the temperature interval which the authors

[2] have analyzed is only 12 K, the  $E_p$ ,  $T$  – functions compared are found to be diametrically opposite in direction. The same goes for the corresponding  $D_2O$ – $H_2O$  solvent isotope effects (IE or  $\delta$ , in later). Suffice it to say that, in authors' [2] opinion,  $\delta V_m^0$  ( $H_2O \rightarrow D_2O$ ) is positive, reaching ca.  $7 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$  at  $T = 293.15 \text{ K}$ . However, going to the data reported in [3], this quantity becomes to be negative, being equal to ca.  $-11 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$  at the same temperature.

Such inconsistencies in results of studying the system ( $D_2O + HMT$ ) can lead not only to contradictory (and, as often happens, to erroneous) results, but also to ambiguous conclusions on the nature of the solute hydration and other intermolecular interactions in the aqueous solutions of interest. As a result, in the interpretation of standard volume-related IEs in aqueous solutions of HMT, the authors [2,3] approached differently the explanation of arising packing effects [1].

Hence, as was concluded in my recent comments [1], *the authentic nature of the volume and volume-isotope effects observed at dissolving HMT in aqueous media still remains unclear*. To derive more reliable and detailed inferences, the additional high-precise densimetric study of HMT solutions in  $H_2O$  and  $D_2O$  within a wide temperature range should be performed. These reasonings have predetermined the main goal of the present investigation. Here, I have attempted to establish a “true pattern” of volume-related (packing) changes in the HMT hydration complex under influence of H/D isotopic substitution in the solvent molecules and temperature.

\* The Laboratory of Thermodynamics of Solutions of Non-electrolytes and Biologically Active Substances, Institute of Solution Chemistry, Russian Academy of Sciences, 1, Akademicheskaya Str., Ivanovo 153045, Russian Federation.

E-mail address: [evi@isc-ras.ru](mailto:evi@isc-ras.ru).

## 2. Experimental

The chemical sample descriptions are presented in Table 1.

After additional purification (see Table 1), the HMT sample was dried for two days under vacuum at  $T = 350$  K (its melting point is ca. 553 K [4]). Then the sample was stored (after and before experiments) in a light-proof vacuum desiccator over  $P_2O_5$ . The pre-deionized and twice distilled water with natural isotopic composition and specific conductivity ( $\kappa$ ) of  $1.3 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$  was used for the solution preparation. Heavy water ( $D_2O$ ) with  $\kappa = 3.0 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$  was used as such (Table 1). The deuterium content in  $D_2O$  was checked by density (up to 0.02 atom % D) using the additive scheme and Kell's data [5] for the absolutely deuterium-substituted water. The residual  $H_2O$  content in heavy water was taken into account in the calculation of the  $D_2O$  molar mass,  $M_{1,D}$ , while preparing the H/D isotopically distinguishable aqueous solutions of HMT.

The solutions under study were prepared by weighting under air-tight conditions using an AND GH-202 type analytical balance (Japan), with an uncertainty of  $1 \times 10^{-5} \text{ g}$ . The content of HMT was expressed in the form of aquamolality,  $m_{aq}$ , which is defined by the number of moles of a solute per 55.50843 mol of  $D_2O$  or  $H_2O$  [6–9]. This concentration scale is of crucial importance for interpretation of thermodynamic functions of transfer including corresponding IEs [6,8,9]. The overall uncertainty in  $m_{aq}$  was estimated to be  $2 \times 10^{-5} \text{ mol}$  per  $55.50843 M_{1,H(D)}$ , at worst. That is, the number at the fifth decimal place in  $m_{aq}$  is trustworthy.

The solution densities,  $\rho_s$ , were measured using an Anton Paar DMA 5000 M densimeter (Austria) with oscillating U-tube. During the experiments, the temperature of measuring cell of ca.  $1 \text{ cm}^3$  volume was kept constant to 0.01 K at each of steady-state temperatures,  $T = (278.15, 288.15, 298.15, 308.15, \text{ or } 318.15) \text{ K}$ . All measurements were carried out within  $p = (99.6 \pm 0.8) \text{ kPa}$ . A standard two-point calibration with freshly prepared water and dry air has been carried out just prior to each series of  $\rho_s$  measurements. The density of water applied in experiments was checked by way of comparing it with the “Ultra pure water” density standard (Anton Paar) whose  $\rho_{1,H}$  values are in compliance with those from the IAPWS Formulation 1995 tables [10]. According to testing results, the values of  $\rho_{1,H}$  for examined samples of water were different from reference those by  $0.005 \text{ kg} \cdot \text{m}^{-3}$ , or lesser. Under such conditions, five-fold measurements of  $\rho_s(m_{aq})$  were reproducible to within  $0.005 \text{ kg} \cdot \text{m}^{-3}$ . Given the HPLC data, impurities of the HMT sample would be changed the solution density at worst by  $0.003 \text{ kg} \cdot \text{m}^{-3}$ . The same goes for the influence of errors at preparing the desired solute concentration. Besides, to check the device operability, the densities of dilute aqueous solutions of the high-purified urea (U: Merck; assay:  $\geq 99.95 \text{ wt}\%$ ) being taken as the “calibration standard” were measured additionally at  $T = 298.15 \text{ K}$ . Comparing the reliable literature values [11–13] with ours for ( $H_2O + U$ ) showed that the existing differences in  $\rho_s$  among them do not exceed  $0.006 \text{ kg} \cdot \text{m}^{-3}$ . Thus, given the influence of all possible factors, the overall uncertainty

in measuring  $\rho_s(m_{aq})$  did not exceed  $0.02 \text{ kg} \cdot \text{m}^{-3}$ . The experimental procedure as well as apparatus design were detailed elsewhere [8,14,15].

## 3. Results

The results of density measurements are summarized in Tables 2 and 3.

Note that densimetric (volumetric) studies of aqueous HMT solutions at low concentration, of  $< 0.3 \text{ mol} \cdot \text{kg}^{-1}$ , are very scarce. Previously, such data for ( $H_2O + HMT$ ) were derived only at  $T = 278.15 \text{ K}$  or lower temperatures (being close to the temperature of maximum density of water) [16,17]. Furthermore, there are no reports of similar data on  $\rho_s(m_{aq})$  or  $V_{\phi,2}(m_{aq})$  for dilute solutions of HMT in  $D_2O$  at the desired temperatures, except for a few concentration-dependent  $\rho_s$  values found in two works I have discussed previously [1]: at  $m \approx 0.20$  ( $T = 298.15 \text{ K}$ ) in [2] and at  $m_{aq} \approx 0.05$  {from  $T = (288.15 \text{ to } 318.15) \text{ K}$ } in [3].

For computing the apparent molar volumes,  $V_{\phi,2}$ , listed also in Tables 2 and 3, the formula [6,9,15,18] expressing the volume of a binary solution,  $V_s$ , in the aquamolality scale was applied.

$$V_s(m_{aq}) = (55.50843 M_{1,H(D)} + M_2 m_{aq}) / \rho_s = V_{1,H(D)}^* + V_{\phi,2} m_{aq} \quad (1)$$

where  $V_{1,H(D)}^* = 55.50843 M_{1,H(D)} / \rho_{1,H(D)}$  is the volume of a pure water isotopologue in the  $m_{aq}$  scale.

According to inferences [6,18],

$$V_s^E(m_{aq}) = v_{22} m_{aq} + v_{222} m_{aq}^2 \quad (2)$$

where  $V_s^E(m_{aq})$  is the excess volume of a solution per 55.50843 mol of a water isotopologue, and the adjustable parameters (virial coefficients)  $v_{22}$  and  $v_{222}$  can be considered as contributions to  $V_s^E$  being related to the solvent-induced solute – solute interactions with forming pair and triple molecular aggregates [6,18,19].

In turn [9,18],

$$V_s^E(m_{aq}) = V_s(m_{aq}) - V_{1,H(D)}^* - V_2^0 m_{aq} \quad (3)$$

Taking Eqs. (1) to (3) into account, one can obtain the following expression



$$V_{\phi,2} m_{aq} = V_s(m_{aq}) - V_{1,H(D)}^* = V_2^0 m_{aq} + v_{22} m_{aq}^2 + v_{222} m_{aq}^3 + \dots \quad (4)$$

According to Eq. (4), all the inferences concerning the interpretation of  $V_s^E$  are in overall valid for  $V_{\phi,2}$ , too. The  $F$ -testing statistical analysis showed that the contribution of  $v_{222}$  term to  $V_{\phi,2}(m_{aq})$  is to be neglected.

The  $V_2^0$  and  $v_{22}$  quantities as well as their 95%-th confidence interval half-widths being obtained in such way are collected in Table 4.

**Table 1**

Provenance and purity of the hexamethylenetetramine and heavy water examined samples.

Characteristics	Solute (in the individual state)	Water D-isotopologue
Structure (empirical) formula		
Molecular brutto-formula	$C_6H_{12}N_4$	$D_2O$
Molar mass, $M_2 / (\text{g} \cdot \text{mol}^{-1})$	140.1882	20.02762 (100 atom % D)
CAS reg. no.	100-97-0	7789-20-0
IUPAC name	1,3,5,7-Tetraazatricyclo[3.3.1.1 <sup>3,7</sup> ]decane	Deuterium oxide
Source	Sigma-Aldrich Co. Ltd. (puriss. p.a.)	Astrakhim Co., Russia
Initial mass fraction purity	$\geq 0.995$	$\sim 0.9994$
Purification method	Double recrystallization from absolute ethanol followed by washing with cold diethyl ether (at the end stage) <sup>a</sup>	Used as such
Final mass fraction purity	$\sim 0.999$	0.9994 ( $\pm 0.0002$ )
Analysis method	HPLC	FT-IR-spectra, density

<sup>a</sup> According to the procedure [4].

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