



Effect of solvent isotopic substitution and temperature on some standard thermodynamic properties of tetramethylthiourea in H₂O and D₂O: A comparison with aqueous oxygen-containing analogue

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ABSTRACT

Density measurements on solutions of 1,1,3,3-tetramethyl-2-thiourea (TMTU) in ordinary (H₂O) and heavy (D₂O) water were carried out with a precision of 0.02 kg·m⁻³ using the Anton Paar DMA 5000 M vibrating tube densimeter. All experiments were performed within the temperature range between (278.15 and 318.15) K, with a step of 10 K, at the pressure to be (99.6 ± 0.8) kPa. The solute aquamolality, *m*_{aq}, was ranged from 0.01 to 0.06 and 0.04 mol·(55.50843 mol of solvent)⁻¹ respectively in the protiated and deuterated solutions. The standard (apparent at infinite dilution) molar volumes, *V*_x^o, and expansibilities, *E*_{p, x}^o, of the solute as well as volume-related second virial coefficients, *v*_{xx}, were derived from the data on density for each of H/D isotopically distinguishable systems. It was established that, unlike the solutions of 1,1,3,3-tetramethyl-2-urea (TMU) in H₂O and D₂O where the standard volume-isotope effect (IE) is negative over the whole temperature range studied, the $\delta V_x^o(\text{H}_2\text{O} \rightarrow \text{D}_2\text{O})$ value for TMTU undergoes a negative-to-positive sign inversion near of 308 K. The same goes for the previously evaluated results on the enthalpy-isotope effect of TMTU hydration. The *v*_{xx} quantities and corresponding IEs are negative, which indicate that the solute studied should have a prevailing structure-making effect on the aqueous surroundings. However, based on the Hepler's criterion, neither structure-making nor structure-breaking effects do not have any predominating influence on the solvation process of TMTU in H₂O or D₂O.

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1. Introduction

The fully *N*-methylated thiourea derivative or 1,1,3,3-tetramethyl-2-thiourea (hereinafter, TMTU), similarly to the related carbonyl-containing compound (1,1,3,3-tetramethyl-2-urea or TMU), is of great interest in a number of branches of physics and chemistry. Particularly, it is actual in the field of construction of nanostructured materials and design of materials with large off-resonance nonlinear optical (NLO-) responses [1,2]. TMU and TMTU are the simple “amide-like” solutes with two kinds of functional moieties (>C=S or >C=O and >N—CH₃) which perturb the aqueous environment in different ways and generate the distinguishable solute–solvent interactions [2–6]. It makes possible to employ them as the “model compounds” for studying the effect of oxygen → sulphur substitution on the solute–solvent interaction in bioactive aqueous media. This effect is influenced by both the “topography” of hydrophobic (methyl) substituents and the hydrogen-bonding ability of proton-donor/acceptor groups of a hydrated solute molecule [2–7].

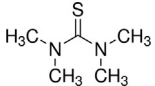

However, unlike aqueous TMU, the hydration behavior of TMTU is far less explored.

With a viewpoint of studying the thermodynamics of hydration process, only temperature-dependent experimental data on the standard (partial at infinite dilution) enthalpic characteristics, $\Delta_{\text{sol}(v)}H_x^o$, for TMTU in water isotopologues (H₂O and D₂O) are reported in the literature [2,5]. In turn, we are not aware of works where the results of determination of volume-related properties for TMTU as a solute in ordinary or heavy water are described, at least at one of temperatures (e.g. at *T* = 298.15 K, as is customary).

The volumetric properties of aqueous TMTU/TMU solutions may be interesting primarily to derive knowledge of structure-packing transformations induced by the solute hydration [6]. In the given context, the standard molar volumes, *V*_x^o (≡ *V*_{φ, x}[∞] = \bar{V}_x^{∞}), and isobaric expansibilities, *E*_{p, x}^o = (∂*V*_x^o/∂*T*)_p, of a solute are fundamentally important due to their independence of the composition effect [8–11]. Furthermore, as we have shown earlier [6,12–16], the experimental approach based on a combination of methods of the high-precision densimetry and the solvent H₂O-by-D₂O isotope substitution is proved to be more informative because a deuteration process is quantum in nature [17–19]. Due to

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Table 1
Provenance and purity of 1,1,3,3-tetramethyl-2-thiourea and heavy water specimens.

Characteristics	Solute	Solvent D-isotopologue
Structure formula and abbreviated name		
Molecular brutto-formula	C ₅ H ₁₂ N ₂ S	D ₂ O
Molar mass, $M_2 / (\text{g} \cdot \text{mol}^{-1})$	132.2298	20.02762 ^a
CAS reg. no.	2782-91-4	7789-20-0
IUPAC name	1,1,3,3-Tetramethylthiourea	Deuterium oxide
Source	Sigma-Aldrich Co. (St. Louis, USA)	Astrakhim Co. (St. Petersburg, Russia)
Initial mass fraction purity	≥0.98	≥0.999 ^b
Purification method	Triple recrystallization from the absolute ethanol (Fluka, puriss) ^c	–
Final mass fraction purity	≥0.999	–0.9992 ^d
Analysis method	HPLC	FT-IR-spectra, density

^a With the 100% deuterium content.

^b With the natural ¹⁸O content (according to a manufacturer certificate).

^c According to the procedure described in [2,5,22].

^d The uncertainty in the deuterium content to be ±0.01 mass %.

differences in the vibrational and donor-acceptor properties of ordinary and heavy water, D-bonds being formed in aqueous media are stronger but more susceptible to destruction under the influence of solute molecules and temperature compared to the similar H-bonds [18,20,21]. Therefore the given approach allows one to establish or clarify (at the molecular level) the role of hydrogen bonds and hydrophobic effects in structure-forming process being manifested in volumetric characteristics of a solute and/or a solution on the whole. Hence, replacing H₂O with D₂O, it is important using the high-purified solute/solvents of the same quality and carrying out the densimetric measurements under the same conditions.

As a part of our efforts to obtain information on the temperature-dependent thermodynamic effects induced by dissolution of TMU and TMTU in H/D isotopically distinguishable aqueous media [5], we report here new results of the densimetric study of solutions of low-soluble TMTU in H₂O and D₂O. All density measurements were carried out at five temperatures from (278.15 to 318.15) K, with a step of 10 K, and at $p = (99.6 \pm 0.8)$ kPa. The V_x^o and $E_{p,x}^o$ values as well as volume-related virial coefficients for pair solute–solute interactions, v_{xx} , were derived from the density data for each of H/D isotopically distinguishable systems being compared.

2. Experimental

2.1. Chemicals

The chemical sample descriptions are given in Table 1. The purified sample of TMTU was dried to constant mass under reduced (down to ~10 Pa) pressure at $T \approx 300$ K [5] and then it was stored (after and before experiments) in a light-proof vacuum desiccator over P₂O₅. The samples' melting point derived with a differential scanning calorimeter NETZSCH DSC 204 F1 Phoenix (Germany) was found to be (350.7 ± 0.5) K. This result is in good agreement with the value of (350.4 ± 0.5) K being reported previously [22].

The pre-deionized and twice distilled water with natural isotopic composition was used for solutions preparation. Its specific conductivity, κ , was 1.3×10^{-6} S·cm⁻¹. Heavy water with $\kappa = 1.2 \times 10^{-6}$ S·cm⁻¹ was used as such (see Table 1). The deuterium content in heavy water was tested (up to ±0.01 at.% D) using the procedure [18] based on the comparison of obtained data on density, $\rho_{w,D}$, with those for “reference” heavy water containing 100 at.% D at the temperature desired [23]. The residual H₂O content in heavy water was taken into account in the calculation of the D₂O molar mass, $M_{w,D}$, while preparing the H/D isotopically distinguishable aqueous solutions of TMTU.

2.2. Solutions preparation

The aqueous solutions of interest were prepared by weighting under air-tight conditions using an AND GH-202 type analytical balance (Japan), with an uncertainty of $\pm 1 \times 10^{-4}$ g. For these purposes, the hermetically sealed glass flasks of a 40 cm³ volume being placed into a dry transparent glove-box were employed. The content of TMTU 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 D₂O or H₂O [14–16,24–26]. The factor of 55.50843 being equal to the number of H₂O moles in 1 kg of water is introduced in order for m_{aq} and molality, m , in the aqueous medium to coincide numerically. Applying the m_{aq} scale is necessary in order to allow the proper comparison of solution densities, ρ_s , and apparent molar volumes of a solute, $V_{\phi,x}$, in the presence of equal numbers of H₂O and D₂O molecules. This is of crucial importance for interpretation of the thermodynamic functions of transfer such as the corresponding D₂O–H₂O solvent isotope effects (IEs or δ , in later). Also, worthy is noting that using the given scale allows reduce an error in the definition of $V_{\phi,x}$ at high dilutions [14–16,27]. Given the fact that the solubility of TMTU in water is rather low (about 0.2 mol·dm⁻³ at room temperature [3]),¹ m_{aq} was ranged in our case only up to 0.057 and 0.038 mol·(55.50843 $M_{w,H(D)}$)⁻¹ in H₂O and D₂O, respectively. Herewith the overall uncertainty in m_{aq} was estimated at worst to be $\pm 4 \times 10^{-5}$ mol per 55.50843 $M_{w,H(D)}$, i.e. the number at the fifth decimal place in m_{aq} is trustworthy.

2.3. Density measurements

The solution densities, ρ_s , were measured using a hermetically sealed high-precision densimeter Anton Paar DMA 5000 M (Graz, Austria) with oscillating U-tube. The apparatus is provided with the automatic viscosity correction and operated under the static mode. During the experiments, the temperature of measuring cell of volume of about 1 cm³ was kept constant to ±0.01 K (with the repeatability of $\pm 2 \times 10^{-3}$ K) at each of five steady-state temperatures: (278.15, 288.15, 298.15, 308.15, or 318.15) K. All measurements were carried out within $p = (99.6 \pm 0.8)$ kPa. The special attention was paid to the calibration procedure. Initially, a standard two-point calibration with freshly prepared water and dry air has been carried out just prior to each series of $\rho_s(m_{aq})$ measurements. The temperature-dependent data on water density, $\rho_{w,H}$, were assumed to be those of the IAPWS Formulation 1995 [28]. The quality of “local” water being applied in the experiments

¹ The TMTU solubility in heavy water is even lower, presumably by a quarter [18].

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