Journal of Molecular Liquids 248 (2017) 48–52

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Short Communication

Some comments on the paper "Effect of temperature on the partial molar volumes and viscosities of two macrocyclic aminals in water and deuterium oxide" by Carmen M. Romero and Holman J. Mesa [Journal of Molecular Liquids, 242 (2017) 244–248]

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ARTICLE INFO

Article history:
Received 21 August 2017
Accepted 27 September 2017
Available online 10 October 2017

Keywords:
Hexamethylenetetramine
Standard volume and expansibility
Ordinary and heavy water

ABSTRACT

Recently, the above authors presented data on the apparent molar volumes and viscosities of solutions of two macrocyclic aminals, hexamethylenetetramine (HMT) and its dodecane-based analogue (TATD), in ordinary and heavy (D_2O) water at four temperatures within a quite narrow interval from 293.15 K to 305.15 K. Noting the reported experimental results for TATD in the deuterium-substituted aqueous medium are of undoubted interest from the viewpoint of novelty of them, I found it necessary to debate the reliability of corresponding data for HMT. The point is that the authors did not consider it possible comparing their data on volume-related properties of the system (D_2O + HMT) with those being available in the literature [Yu.P. Pankratov, V.K. Abrosimov, Russ. J. Phys. Chem. 71 (1997) 1263–1266]. Herewith, discussing the standard (at infinite dilution) molar volumes of HMT in ordinary water, the authors under comment (C.M. Romero and H.J. Mesa) have repeatedly referred to the specified work. Therefore, the question arose whether the existing data sets on volumetric characteristics of HMT in the H/D isotopically distinguishable aqueous media agree with each other. In this regard, using the results of mentioned and other researchers, I have carried out the comparative analysis of temperature-dependent values of standard molar volumes and expansibilities of HMT in both H_2O and D_2O. Two main points relating to the problem were considered here: how plausible is each of the compared "author's" volumetric characteristics relating to the H/D isotopically distinguishable aqueous media and how it is correlated with the predicted nature of the HMT hydration. Being found in the above sources, the pronounced inconsistencies in results of studying the standard molar volumes and expansibilities of the solute in both (H_2O + HMT) and (D_2O + HMT) point out the necessity for additional high-precise densimetry investigations of these binary liquid systems.

I read with great interest the recent paper of the above authors (C.M. Romero and H.J. Mesa) entitled the "Effect of temperature on the partial molar volumes and viscosities of two macrocyclic aminals in water and deuterium oxide" [1]. In the specified study, the apparent molar volumes and the viscosities of solutions of 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane or hexamethylenetetramine (HMT) and 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD) in water H/D isotopologues (H_2O and D_2O) were determined from the density data at T = (293.15, 298.15, 300.15 and 305.15 K) and under ambient pressure.

The former of such aminals, HMT (see in Fig. 1), being the well-known antiseptic pharmaceutical (*hexamine* or *urotropine*), is a thoroughly studied compound in both the crystalline and dissolved (hydrated) states. In turn, the data on volume- and viscosity-related properties for aqueous TATD solutions are virtually scarce in the open literature. Therefore the results reported in [1] for the binary systems (H_2O + TATD) and (D_2O + TATD) would apparently be of important value in completing the information on thermodynamic and physicochemical properties of the aqueous aminals in question. I value the efforts of the authors [1] to contribute important fundamental data on the aqueous TATD, whose molecular structure is more complicated with a stereochemical viewpoint. Therefore there is no problem with the data that Romero and Mesa [1] have presented for both TATD-containing systems. The same goes for their results of viscosimetric measurements for the HMT solutions in heavy and ordinary water, too.

Meanwhile, our scientific group has also investigated some thermodynamic properties of the H/D isotopically distinguishable aqueous

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https://doi.org/10.1016/j.molliq.2017.09.125
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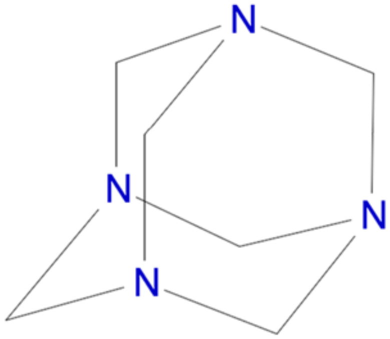

Fig. 1. A simplified structure of the HMT molecule.

solutions of HMT including the volume characteristics of this polycyclic compound as a solute [2–5]. Hence it seemed appropriate to compare the discussed data from [1] with the previous those. I found it necessary to debate here a "scientific value" of volume-related characteristics for HMT derived from the density measurements of its solutions in water isotopologues. Apart from some "formal" remarks, I have two substantial objections. Primarily, I have decided to write this comment because Y.P. Pankratov and V.K. Abrosimov [2] published the similar paper two decade ago, whose data on volumetric properties of (D_2O + HMT) for unknown reason remained unnoticed by the authors of the paper being titled above. Herewith, analyzing the standard (partial at infinite dilution) molar volumes of HMT in ordinary water, the authors [1] have repeatedly referred to the paper [2]. Secondly, no the authors [1] cite the separate parts of the work [2] in which the influence of solvent H/D isotope substitution on the thermodynamic quantities of interest is discussed and they did virtually neglected the analysis of the corresponding isotope effects (hereinafter, IE or δ) during discussion of own results.

Using only tabulated values of molar volumes, V_2^{o}, the authors [1] have compared their results with selected literature data for (H_2O + HMT) [6,7] at two temperatures being 298.15 K and 305.15 K in a very narrow temperature range equal to 12 K (!). What is hard to understand is why the authors [1] have not preferred the temperatures 303.15 K and 308.15 K instead of 300.15 K and 305.15 K, respectively, as is customary in such cases for convenience of comparing [2,6,8]? And, why they have not mentioned the V_2^{o} values for (D_2O + HMT) from the work [2], at least at a sole coinciding temperature (T = 298.15 K)?

Unfortunately, no data are presented as a graphic material in the paper in question. I do not fault the authors [1] for not depicted graphically the results derived. However this strongly complicates a comparative analysis of the results [1,2] being discussed here. To ensure such a comparison, I have plotted the temperature-dependent functions for V_2^{o} (Fig. 2*a*–*b*) and standard molar expansibilities, $E^{\mathrm{o}}_{p,2} = (\partial V_2^{\mathrm{o}}/\partial T)_p$ (Fig. 3*a*–*b*). A comprehensive comparison is presented in Figs. 2*a* and 3*a*, juxtaposing the data on V_2^{o} and $E^{\mathrm{o}}_{p,2}$ for the system (H_2O + HMT) from the works [1,2] with similar values existing in other literature sources and being critically evaluated as "reference" ones.

As can see from Figs. 2*a* and 3*a*, there is no obvious compliance between the data [1,2] being compared at the same temperature. Herewith if the V_2^{o} values reported by Pankratov and Abrosimov [2] are systematically higher lying (but only by ~1 $cm^3 \cdot mol^{-1}$) relative to most of literature values listed in Fig. 2*a*, the corresponding quantities from [1] are dramatically increasing with temperature. Suffice it to say that, in the last case, the distinction in V_2^{o} makes up >2 $cm^3 \cdot mol^{-1}$ at finite temperatures compared with others. The same goes for the data on $E^{\mathrm{o}}_{p,2}$ being depicted in Fig. 3*a*, with the only difference that the results [2] lie into the limits of average-weighted those whereas the results of Romero and Mesa [1] seem to be absurd on the background of the set of fairly reliable literature values.

The more ambiguous situation is observed for the data on V_2^{o} and $E^{\mathrm{o}}_{p,2}$ being presented in Figs. 2*b* and 3*b* for the system (D_2O + HMT). The conformity between the results under comparison cannot be named reasonable. So, the quantities of V_2^{o} reported by the authors [2] are catastrophically lower lying (by ~11 $cm^3 \cdot mol^{-1}$, on an average!) compared to the data of Romero and Mesa [1], at all the temperatures being studied (see Fig. 2*a*). In turn, according to [1], the $E^{\mathrm{o}}_{p,2}$ value for HMT in the deuterated aqueous medium is abruptly ascending as the temperature is rising while, in the opinion of [2], the $E^{\mathrm{o}}_{p,2} - T$ function is to be diametrically opposite in direction (see Fig. 3*b*). The values in comparison are satisfactory agreed between themselves only at separate temperatures close to a crossing point at $T \approx 303$ K. (It should be also take into account the "scaling effect" when Fig. 3*a* and *b* are comparEd.)

As it follows from the figures, the evaluated differences in the thermodynamic (packing-related) characteristics under discussion are very significant. One can expect that such a discrepancy in both V_2^{o} and

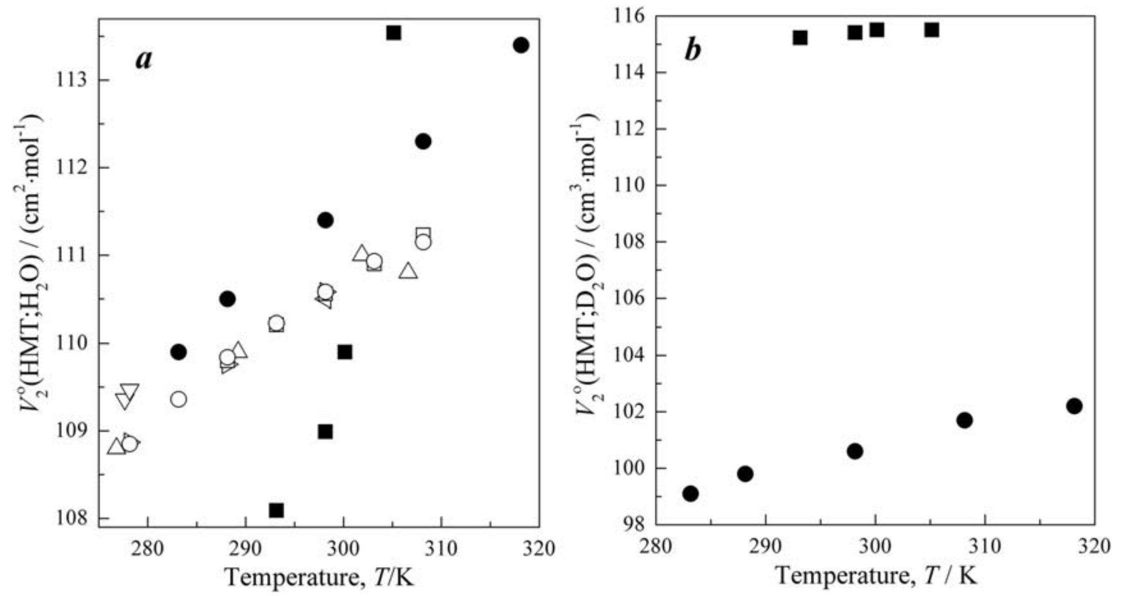

Fig. 2. The standard molar volumes of HMT in ordinary water (***a***) and heavy water (***b***) as a function of temperature: ■, Romero & Mesa [1]; ●, Pankratov & Abrosimov [2]; □, Blanco et al. [6[; □, Afanas'ev [8]; Δ, Crescenzi et al. [7]; ∇, Clavijo Penagos & Blanco [9]; ⊲, White [10]; ⊳, Herrington & Mole [11].