



ELSEVIER

Contents lists available at ScienceDirect

## Journal of Molecular Liquids

journal homepage: [www.elsevier.com/locate/molliq](http://www.elsevier.com/locate/molliq)

## Structural changes of water caused by non-electrolytes: Volumetric and compressibility approach for urea-like analogues

Jarosław Wawer\*, Joanna Krakowiak

Department of Physical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza Str. 11/12, Gdańsk 80-233, Poland

## ARTICLE INFO

## Article history:

Received 27 September 2017  
 Received in revised form 26 February 2018  
 Accepted 28 February 2018  
 Available online 6 March 2018

## Keywords:

Density  
 Speed of sound  
 Apparent molar volume  
 Apparent molar isentropic compression  
 Hydrophobic hydration

## ABSTRACT

Hydration of thiourea (TU), hydroxyurea (HU, hydroxycarbamide), acetone (AC, 2-propanone) and dimethyl sulfoxide (DMSO) has been investigated with the help of the volumetric and compression measurement. The apparent molar volumes and the apparent molar isentropic (adiabatic) compression have been calculated from the density and speed of sound data at temperatures ranging from 288.15 to 308.15 K at atmospheric pressure (0.1 MPa). From these data the standard partial molar volumes and the standard partial molar isentropic compressions have been calculated.

The properties of the hydration spheres formed around investigated solutes have been characterised based on four parameters: (i) empirical slope for the dependency of the apparent molar volume on the concentration, (ii) difference between standard partial molar volume and van der Waals volume, (iii) standard partial molar compression, (iv) temperature dependency of the standard partial molar compression. The obtained results have been discussed and compared with the solvation properties of the N-alkyl derivatives of urea.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Low molecular weight compounds play a crucial role in a regulation of biological systems. Among others, the intracellular osmolytes are particularly interesting due to their unique function. They accumulate in cells in a response for the harsh environmental conditions and influences the protein stability [1]. The newest report suggests [2] that similarity of the solvation sphere of co-solute and the hydration shell of protein decides whether the compound stabilise or destabilise the protein. In this context the detailed description of how the presence of the solute changes the water properties is important for better characterisation of biological processes.

Our previous studies show [3–5] that the comparison made for the short series of derivatives cannot provide all answers. Thus, it is essential to perform the measurements for the broader range of the solutes.

The aim of the current study is to compare the solvation properties of the compounds in which some of the atoms have been substituted by different residues. This work, among other problems, discusses the iceberg model of the hydration of apolar compounds [6]. Despite the passing years, the validity of this classical interpretation of the hydrophobic effects is still questioned and tested [7–10].

The advantage of the presented approach is the simplicity of the interpretation of measured macroscopic parameters i.e. the standard partial molar volumes  $V_{\phi}^0$  and standard partial molar isentropic compressions  $K_{S,\phi}^0$ . The  $V_{\phi}^0$  describes the change of the volume of the solution when one mole of solute is added to the infinite amount of pure solvent. This parameter depends on the size of the unsolvated solute and the structural changes of the solvent. The  $K_{S,\phi}^0$  characterises the resistance of the infinitely dilute solution to the mechanical stress in the comparison to the pure solvent, and it is recalculated for one mole of solute. The qualitative interpretation of the sign of  $K_{S,\phi}^0$  is simple. The negative value of the standard partial molar compression means that the introduction of the solute reinforces the solution. The positive value of  $K_{S,\phi}^0$  is a proof that the structure of the solution becomes more loose [11–13]. Additionally, we extended our studies and investigated the concentration and temperature dependencies of the volumetric and compression related parameters. In the current work we wanted to refrain from making assumptions and analyse directly the obtained parameters.

The volumetric and compressibility measurements have been performed for number of systems including these discussed in the present work [14–24]. However, the above mentioned papers are limited to one temperature or report only one parameter e.g. standard partial molar volume. For these reasons, the description of the hydration is incomplete. The investigations covering wider temperature range and examining the concentration dependencies are rare [15,21,25,26]. Moreover, some of these papers do not report the

\* Corresponding author.

E-mail address: [jarwawer@pg.edu.pl](mailto:jarwawer@pg.edu.pl) (J. Wawer).

quantities for infinite dilution [25,26]. The two latter works, and the other ones [27,28] in fact address scientific questions which are far different from these in present work. Similar situation is for articles analysing the excess molar quantities [29–31]. These works present the data over wide concentration ranges. As a result there are insufficient numbers of experimental points in the low concentration of the solute and the estimation of the standard partial molar quantities is impossible. There are far less experimental studies of the compressions. To our best knowledge, the volumetric and compression data for hydroxyurea have been measured and presented for the first time.

## 2. Experimental

### 2.1. Materials and solutions preparation

The source and the grade of the chemicals are shown in Table 1. The chemicals were used as received without further purification. Water was distilled and degassed by boiling prior preparation of solutions. The solutions were prepared by weight using an analytical balance (Radwag WAA 40/160/X/1, Poland) with the precision of 0.1 mg. All solutions were prepared by weighted dilution of stock solution in one day. The sample containers were hermetically sealed and densities of the solutions and sound speeds were measured in a following days. The standard uncertainty of the molality determination was around  $0.0001 \text{ mol} \cdot \text{kg}^{-1}$ .

### 2.2. Density and speed of sound measurements

The densities and speed of sound values were determined by Anton Paar DSA 5000 M densimeter. The precisions of the measurements are equal  $1 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and  $0.1 \text{ m} \cdot \text{s}^{-1}$  for density and speed of sound, respectively. The “accuracies” of the measurements declared by the apparatus manufacturer are  $5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and  $0.5 \text{ m} \cdot \text{s}^{-1}$ . However, to obtain more realistic values of the uncertainty one need to take into account the discrepancies caused by the systematic errors and variation of the sample impurities caused by the differences between solvent batches. Based on the measurements made for the pure water we estimate the uncertainty of the density measurements to be equal  $35 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ . For the sound speed, we accept the value declared by the manufacturer ( $0.5 \text{ m} \cdot \text{s}^{-1}$ ).

Temperature was stabilised at 288.15, 293.15, 298.15, 303.15 and 308.15 K by in-built Peltier temperature control unit with the precision of  $1 \cdot 10^{-3} \text{ K}$ .

Before the series of measurements the apparatus has been calibrated using the standard solvent (water) delivered from the Anton Paar supplier. Densities and sound speeds for pure acetone and dimethyl sulfoxide are collected in Table 2. For each series of solutions, the densities and sound speeds for the pure water used for the solutions preparation were measured. The average values resulting from these measurements are presented in Table 2. Obtained values are in good agreement with the literature data.

In order to refer the measured densities and sound speeds to the same reference we used following equations:

$$d = d^{\text{exp.}} - d_0^{\text{exp.}} + d_0 \quad (1)$$

$$u = u^{\text{exp.}} - u_0^{\text{exp.}} + u_0 \quad (2)$$

where:  $d^{\text{exp.}}$  and  $u^{\text{exp.}}$  are the experimental values of densities and sound speeds measured for the solutions,  $d_0^{\text{exp.}}$  and  $u_0^{\text{exp.}}$  are the experimental values of densities and sound speeds measured for the pure water used for solutions preparation. The  $d_0$  and  $u_0$  are the reference values of densities and sound speeds for the pure water taken from the literature. The reference values for pure water and the recalculated values for the pure components are presented in Table 2. The obtained  $d$  and  $u$  values for the solutions are collected in Tables 3, 6–9.

### 2.3. Volume of molecule calculation

The van der Waals volumes of the solute molecules were calculated using HyperChem Release 8.0.3 for Windows (semiempirical method AM1).

## 3. Results

### 3.1. Volumetric properties

For all solutes, except acetone, densities of the mixtures increase as the concentration of solute increases. In the case of the acetone solution, the density of the solution decreases with the increase of the concentration of the less dense liquid. Our earlier reports show that this behaviour is not a rule, the density of the solution of tetramethylurea (TMU) [3,5] increases as the concentration of the less dense component (i.e. TMU) increases.

From the obtained densimetric data, the apparent molar volumes  $V_\phi$  were calculated according to the equation:

$$V_\phi = \frac{M_2}{d} - \frac{d - d_0}{mdd_0} \quad (3)$$

where:  $M_2$  is the molar mass of the solute,  $m$  is the number of moles of the solute per kilogram of solvent (molality),  $d$  is the density of the solution calculated from the Eq. (1) and  $d_0$  is the reference density of pure water.

The obtained values of  $V_\phi$  are presented in the supplementary materials (Tables S1–S4). We assumed that the concentration dependencies of  $V_\phi$  for all investigated systems are linear (see Fig. 1 for thiourea as an example). The apparent molar volume of TU increases with the concentration. For HU, the  $V_\phi$  is almost insensitive to concentration changes. In the case of acetone and dimethyl sulfoxide the apparent molar volumes decrease as the concentration of the solute increases.

**Table 1**  
Source and purity of chemicals used in this work.

Chemical	Chemical formula	Molar mass/( $\text{g} \cdot \text{mol}^{-1}$ )	Source	Purity <sup>a</sup>	CAS number
Thiourea (TU)	( $\text{NH}_2$ ) <sub>2</sub> CS	76.1222	Sigma Aldrich	≥ 0.99	62-56-6
Hydroxyurea (HU)	$\text{NH}_2\text{CONHOH}$	76.0550	Sigma	≥ 0.98	127-07-1
Acetone (AC)	( $\text{CH}_3$ ) <sub>2</sub> CO	58.0800	POCh SA	≥ 0.995	67-64-1
Dimethyl sulfoxide (DMSO)	( $\text{CH}_3$ ) <sub>2</sub> SO	78.1350	POCh SA	≥ 0.99	67-68-5

<sup>a</sup> Assay in mass fraction, as declared by the supplier.

Download English Version:

<https://daneshyari.com/en/article/7842511>

Download Persian Version:

<https://daneshyari.com/article/7842511>

[Daneshyari.com](https://daneshyari.com)