Hydration of urea and its derivatives – Volumetric and compressibility studies

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The densities and sound velocities at T = (288.15, 293.15, 298.15, 303.15 and 308.15) K have been measured for aqueous solutions of urea, N,N-dimethylurea, N,N-diethylurea, N-propylurea, N-butylurea. From these data the apparent molar volumes, V_Φ, the apparent molar isentropic compressions, $K_{S,\Phi}$, and the Passynski solvation numbers of solutes have been determined. The concentration dependencies of the calculated quantities, their limiting values and temperature characteristics are discussed in terms of (solute + solvent) and (solute + solute) interactions.

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1. Introduction

The presented work is a part of our systematic study on the volumetric and acoustic features of the osmolytes, *i.e.* molecules strongly influencing the physico-chemical behavior of proteins. Urea is a compound that is highly active in a variety of biological processes and has been known as protein denaturing agent for many years. The properties of alkyl derivatives of urea are similar and all these compounds are regarded as protein destabilizers [1,2]. The mechanism by which urea denatures proteins in aqueous solutions is still not clarified. It has been proposed that osmolytes interact with macromolecule directly or influence the protein stability through surrounding water by modification of its properties. By contrast, alkylureas are effective in certain conditions in the refolding of denatured proteins. From here, the change of the structure and hydrodynamics of the solvent in the presence of urea and its derivatives [3] have fundamental importance in understanding of the denaturation process of protein [4].

The volumetric and acoustic techniques have been extensively used in understanding of intermolecular interactions in liquids, because of their sensitivity to the entire spectrum of (solute + solvent) and (solute + cosolute) interactions [5–8]. The limiting apparent molar values can be interpreted in terms of (solute + solvent) interactions. Whereas, the specific (solute + solute)

interactions can be revealed from concentration change of the apparent volume.

The present work was undertaken to study volumetric and acoustic properties of urea (U), N,N-dimethylurea (N,N-DMU), N,N-diethylurea (N,N-DEU), N-propylurea (PU) and N-butylurea (BU) in aqueous solutions at low concentration. The apparent molar volume, V_Φ, isentropic compressibility, κ_S, hydration number and apparent molar adiabatic compression, $K_{S,\Phi}$, were obtained from measured densities and speed of sound at T = (288.15, 293.15, 298.15, 303.15 and 308.15) K. The standard partial molar volumes and compressions were estimated by extrapolation of the apparent molar quantities to infinite dilution. The obtained parameters are discussed in terms of (solute + solvent) and (solute + solute) interactions.

The authors have presented the volumetric and acoustic parameters for urea and N-butylurea aqueous solutions in the previous article [9] but the speed of sound measurements were limited only to one temperature 298.15 K. In this study more advanced instrument was used and the acoustic parameters were determined in the entire temperature range. The results obtained in earlier work [9] were critically revised.

2. Experimental

2.1. Materials

Source and grade of the chemicals used in this work are presented in table 1. Urea (U), N,N-dimethylurea (N,N-DMU),

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TABLE 1

Source and grade of chemicals used in this work.

Chemicals	Source	Purity[a]
Urea (U)	Riedel-de Haën	⩾0.995
n-Propylurea (PU)	Alfa Aesar	⩾0.98
N,N-dimethylurea (DMU)	Aldrich	⩾0.99
N,N-diethylurea (DEU)	Aldrich	⩾0.97
n-Butylurea (BU)	Fluka	⩾0.99

[a] Assay in mass fraction.

TABLE 2

The calculated van der Waals volume, V_{vdw}, the solvent accessible volume, V_{sa}, and the solvent accessible surface area, S_{sasa}, for the studied solutes.

Solute	$10^6 \cdot V_{vdw}/$ $(m^3 \cdot mol^{-1})$	$10^6 \cdot V_{sa}/$ $(m^3 \cdot mol^{-1})$	$10^{-4} \cdot S_{sasa}/$ $(m^2 \cdot mol^{-1})$
U	30.96	143.38	116.60
PU	60.21	228.10	163.50
DMU	51.24	202.70	149.72
DEU	70.48	257.46	179.07
BU	71.94	272.50	192.45

N,N-diethylurea (N,N-DEU), N-propylurea (PU) and N-butylurea (BU) were dried over P_2O_5 at room temperature for (24 to 48) h without further purification. Water for solution preparation was distilled and then degassed by boiling for about 20 min.

The solutions were prepared by weight using an analytical balance (Radwag WAA 40/160/X/1, Poland) with the precision 0.1 mg.

2.2. Density and sound velocity

The densities of the solutions and the speed of sound were measured using Anton Paar DSA 5000M densimeter with precision of $1.0 \cdot 10^{-3}$ kg · m^{-3} and 0.1 m · s^{-1} for a single measurement of the density and speed of sound, respectively. The values of the speed of sound in studied systems were measured at frequency of 3 MHz. The instrument was equipped with the Peltier-type thermostating unit and temperature was kept constant at (288.15, 293.15, 298.15, 303.15 and 308.15) K with repeatability of ±0.001 K.

2.3. Surface and volume of molecule

The solvent accessible volumes of the studied solutes as well as van der Waals volume and solvent accessible surface have been calculated by the grid method described by Bodor et al. [10] using the atomic radii of Gavezotti [11], implemented in HyperChem Release 8.0.3 for Windows (Hypercube Inc.) The results of these calculations are presented in table 2.

3. Results

3.1. Density and sound velocity

Tables 3 and 4 present the density and the speed of sound data, respectively, obtained for aqueous solutions of urea (U), N,N-dimethylurea (N,N-DMU), N,N-diethylurea (N,N-DEU), N-propylurea (PU) and N-butylurea (BU) at the temperature ranging from (288.15 to 308.15) K.

The concentration dependencies of the density and speed of sound for all solutions can be described at all measured temperatures by the equation:

$$y = y_0 + A_y m + B_y m^2,\qquad(1)$$

TABLE 3

Densities d of the aqueous solutions of urea and its derivatives for various molality of the solute at different temperatures[a] and at pressure $p \cong 0.1$ MPa.

$m/$ $(mol \cdot kg^{-1})$	$d/(kg \cdot m^{-3})$				
	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K
Urea					
0	999.086	998.201	997.045	995.653	994.043
0.0504	999.922	999.019	997.847	996.442	994.816
0.0807	1000.426	999.511	998.329	996.911	995.281
0.1107	1000.918	999.994	998.802	997.378	995.738
0.1510	1001.581	1000.641	999.436	997.998	996.351
0.2005	1002.391	1001.430	1000.210	998.757	997.097
0.2512	1003.214	1002.229	1000.993	999.529	997.855
Propylurea					
0	999.096	998.206	997.051	995.650	994.036
0.0494	999.566	998.653	997.480	996.069	994.440
0.0790	999.848	998.924	997.740	996.318	994.678
0.1089	1000.134	999.198	998.003	996.573	994.925
0.1484	1000.517	999.564	998.356	996.910	995.249
0.1983	1000.994	1000.021	998.792	997.329	995.652
0.2490	1001.486	1000.493	999.244	997.763	996.069
0.3012	1001.991	1000.974	999.704	998.202	996.489
N,N-dimethylurea					
0	999.095	998.205	997.048	995.653	994.037
0.0526	999.644	998.733	997.562	996.154	994.527
0.0842	999.970	999.051	997.869	996.454	994.818
0.1149	1000.290	999.360	998.171	996.746	995.103
0.1572	1000.728	999.785	998.583	997.148	995.495
0.2104	1001.283	1000.321	999.103	997.653	995.988
0.2629	1001.831	1000.850	999.617	998.153	996.474
0.3180	1002.401	1001.405	1000.153	998.673	996.980
N,N-diethylurea					
0	999.100	998.209	997.054	995.661	994.040
0.0535	999.376	998.462	997.288	995.875	994.243
0.0856	999.546	998.620	997.435	996.012	994.369
0.1181	999.725	998.786	997.589	996.154	994.501
0.1603	999.959	999.002	997.788	996.338	994.672
0.2142	1000.267	999.288	998.052	996.585	994.898
0.2689	1000.589	999.586	998.328	996.837	995.135
0.3254	1000.929	999.905	998.628	997.108	995.381
n-Butylurea					
0	999.126	998.232	997.074	995.678	994.065
0.0486	999.444	998.527	997.349	995.933	994.297
0.0781	999.638	998.707	997.514	996.086	994.438
0.1078	999.835	998.889	997.683	996.243	994.583
0.1473	1000.100	999.134	997.909	996.448	994.774
0.1974	1000.443	999.450	998.201	996.718	995.022
0.2475	1000.782	999.763	998.489	996.985	995.266
0.2986	1001.137	1000.09	998.789	997.259	995.516

[a] Standard uncertainties u are $u(d) = 5.0 \cdot 10^{-3}$ kg · m^{-3}, $u(T) = 0.01$ K and $u(m) = 0.0001$ mol · kg^{-1}.

where m (mol · kg^{-1}) is the molality of a solute (the number of mole of the solute per 1 kg of the pure solvent); y denotes, either, the density of solution d (then y_0 is the density of the pure solvent, d_0) or the speed of sound u (then y_0 is the speed of sound in the pure solvent, u_0); A_y and B_y are the empirical coefficients. The coefficients of the equation (1) and their standard deviations are given in tables 5 and 6. The standard deviation, σ, calculated for all relations is as follows: $\sigma = \left(\sum (Y_{cal} - Y_{exp})^2 / f \right)^{1/2}$ where: Y_{exp} is the value obtained experimentally; Y_{cal} is that calculated from fitted equation and f is the number of degrees of freedom.

Inspection of these data reveals analogously to earlier work [9] impact of the chemical formula of the solute on measured quantities. The steepest change of the density with concentration of a solute is observed for urea solution, and this effect decreases as the size of the molecule increases. The lowest increase in the solution density with solute concentration is determined for N,N-diethylurea. Presence of the solute brings opposite effect on the change of the speed of sound as compared to the density changes. The speed of sound increases with increasing concentration in all