

APPARENT MOLAL VOLUME, APPARENT MOLAL COMPRESSIBILITY, VERIFICATION OF JONES–DOLE EQUATION AND THERMODYNAMIC STUDIES OF AQUEOUS UREA AND ITS DERIVATIVES AT 25, 30, 35 AND 40°C

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ABSTRACT

Ultrasonic, volumetric and viscometric measurements have been performed on urea and its derivatives at 25, 30, 35 and 40°C. These measurements have been used to evaluate some important ultrasonic and thermodynamic parameters, viz. apparent molal volume ϕ_V , partial molal volume ϕ_V^0 , apparent molal compressibility ϕ_K , partial molal compressibility ϕ_K^0 , viscosity B -coefficient of Jones–Dole equation, free energy of activation for viscous flow ΔG , entropy ΔS , and enthalpy of activation ΔH for viscous flow. These parameters have been used to interpret the results in terms of solute–solvent interactions. The structural interactions of urea and its derivatives with water molecules are interpreted successfully.

INTRODUCTION

Aqueous urea and its derivatives are important mixed solvents. They have been the subject of numerous investigations which have ranged widely in scope and purpose [1]. While the thermodynamic properties of these solvent systems have been characterized [2].

Urea and its derivatives are well characterized in water and act as a statistical structure breaker. From the effect of guanidine hydrochloride, urea and its alkyl derivatives upon the structure of water, it was concluded that guanidine hydrochloride and urea molecules behave as a structure breaker for liquid water [3–7].

Subramanian et al. [8] have shown from NMR and specific heat capacity data on aqueous solution of urea and its derivatives, that the relative decreasing order of structure making properties (in water) is: tetramethyl-urea > N , N' -dimethylurea > urea. Finar et al. [9] pointed out that the

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results of proton chemical shift studies on aqueous solution of urea do not agree with those of Subramanian et al. [8], and thus this order for the structure making properties is doubtful. Solvation and hydrophobic hydration of alkyl substituted ureas and amides in *N, N'*-dimethylformamide + water mixtures has been discussed by Rouw et al. [10]. Partial molal volumes of copper sulphate in urea–water solutions has been studied by Blokhra et al. [11]. Apparent molar volumes and heat capacities and corresponding state functions have been calculated by Criss et al. [12]. The conductance of KCl and NaCl in sucrose + water, glucose + water and urea + water mixtures at different temperatures has been measured by Mohanty and Das [13]. The dependence of ultrasonic velocity on structure in a homologous series of non-electrolytes in aqueous medium has been studied by Antosiewicz and Shugar [14]. Apparent molar volumes in mixed salt solutions have been studied by Padova et al. [15]. Partial molar volumes of amino acid derivatives in water have been determined by Shahidi [16].

Interactions of Na^+ , K^+ , Ca^{2+} and Mg^{2+} with D-mannose and D-glucose in aqueous solution has been observed by ultrasonics and has been described [17]. Apparent molal volume, apparent molal compressibility, verification of Jones–Dole equation and free energy change of aqueous D(–)-fructose in the presence of Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions has been described [18].

The thermodynamic studies have been made on ternary systems of electrolytes–non-electrolyte–water, where the non-electrolytes are tert-butanol (TBA) [19–21] and urea (U) [22]. Both the solutes are well characterized in water. TBA acts as a fairly typical hydrophobic solute and U as a statistical structural breaker. Recently Sangaster et al. [23] studied the effect of Na^+ , K^+ and urea on an aqueous solution of sucrose. Apparent molar volumes of aqueous cellobiose solutions have been presented by Herrington et al. [24]. The adiabatic compressibility of non-electrolyte–aqueous solutions in relation to the structure of water and solutions have been calculated by Endo [25].

The structure of a urea + water mixture is of great importance in understanding its protein denaturation. The present study reports the ultrasonic, volumetric and viscometric measurements in aqueous solution of urea and its derivatives at 25, 30, 35 and 40 °C. The temperature dependence studies explain the solute–solvent interaction of urea and its derivatives in aqueous solutions clearly. The alkyl group–water interaction is successfully presented in such a study.

EXPERIMENTAL

The density measurements were performed with a precalibrated pycnometer at 25, 30, 35 and 40 ± 0.01 °C. The estimated error in the density measurements was found to be ± 0.001%.

From the density data, the apparent molal volume ϕ_v of aqueous urea and its derivatives is calculated from eqn. (1).

$$\phi_v = \left(\frac{1000(d_0 - d)}{md_0d} \right) + \left(\frac{M}{d} \right) \quad (1)$$

where ϕ_v is the apparent molal volume of solute, d_0 and d are the densities of solvent and solution, respectively, m is the molality and M represents the molecular weight of the solute. ϕ_v is the linear function of the concentration term and is in good agreement with Masson's equation [26]:

$$\phi_v = \phi_v^0 + S_v^* \sqrt{C} \quad (2)$$

where ϕ_v^0 is the partial molal volume at infinite dilution and is the measure of solute-solvent interaction [27]. It is obtained from the linear plot of ϕ_v vs. \sqrt{C} using the least-squares method. S_v^* is the experimental slope and is the measure of solute-solute interaction.

Ultrasonic velocity (U) measurement has been performed using a variable-path ultrasonic interferometer with a frequency of 2 MHz. The estimated error has been found to be $\pm 0.02\%$. Details of the apparatus are reported elsewhere [28].

The viscosity of the solution was measured using a calibrated, modified Ostwald-type viscometer at 25, 30, 35 and $40 \pm 0.01^\circ\text{C}$. Uncertainty in the viscosity measurements is found to be $\pm 0.01\%$. Viscosity data were analysed in terms of the Jones-Dole equation [27]. Thermodynamic parameters are evaluated from the viscosity values. The extended Jones-Dole equation including the term D has not been extensively studied [29], but was recently discussed for an aqueous system by Desnoyers and Perron [30].

Adiabatic compressibility has been computed from ultrasonic velocity and density data using eqn. (3).

$$\beta_s = 1/U^2d \quad (3)$$

Partial molar compressibility has been deduced from the isentropic apparent molal compressibility using eqn. (4).

$$\phi_K = (1000(\beta_s - \beta_0)/md_0) + \phi_v\beta_s \quad (4)$$

where β_s and β_0 are the compressibilities of the solution and solvent, respectively, d_0 is the density of the medium, ϕ_v represents apparent molal volume and m is the molality of the solution (g l^{-1}). ϕ_K is the apparent molal compressibility which is the linear function of concentration, found to be in good agreement with Masson's equation [26].

$$\phi_K = \phi_K^0 + S_K^* \sqrt{C} \quad (5)$$

where ϕ_K^0 is the partial molal compressibility at infinite dilution and is the measure of solute-solvent interaction [28] and S_K^* is the experimental slope. The value of ϕ_K^0 has been deduced from the linear plot of ϕ_K vs. \sqrt{C} using the least-squares method.

Viscosity measurement was carried out using the Jones–Dole equation

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \quad (6)$$

where η/η_0 is the relative viscosity of the solution and C is the concentration (g l^{-1}). A and B are viscosity interaction coefficients. A represents the contribution from interionic electrostatic forces [29] and B is the measure of order or disorder introduced by the ion into the solvent structure. This constant is specific and is an approximately additive property of ions of an electrolyte at a given temperature, although no satisfactory theoretical treatment has yet been given. By plotting $(\eta/\eta_0 - 1)/\sqrt{C}$ vs. \sqrt{C} the coefficients A and B can be obtained. Such a theory is developed for the coefficient B ; however, it is a manifestation of ion–solvent interactions [30].

Viscosity data have also been used for the calculation of solute activation parameters [28]. The free energy of activation for viscous flow is given by [31,32]:

$$\Delta G^* = RT \ln(\eta V/hN) \quad (7)$$

where h is the Planck constant, N is Avogadro's number and V may be regarded as the volume of one mole of solute particles and is given by the equation

$$V = \left(\frac{1000}{n_1 + \nu n_2} \right) \text{cm}^3 \quad (8)$$

where ν is the number of species into which a solute molecule dissociates and n_2 is the number of moles of solute per litre of solution. The number of moles of solvent n_1 per litre of the solution is given by the equation

$$n_1 = (1000d - n_2 M_2)/M_1 \quad (9)$$

where M_1 and M_2 are the molecular weights of solvent and solute, respectively. By measuring B at different temperatures, enthalpies and entropies of activation can be obtained using eqs. (10) and (11).

$$\Delta S^* = \frac{-d(\Delta G^*)}{dT} \quad (10)$$

$$\Delta H^* = \Delta G^* + T\Delta S^* \quad (11)$$

DISCUSSION

The results can be interpreted in the following way. The positive values of ϕ_V in all the systems indicate the solute–solvent interaction in the solutions. The values of apparent molal volume (ϕ_V) decrease with the increase in solute (urea and its derivatives) concentration. Such behaviour indicates that the solute–solvent interaction decreases with the increase in concentration of urea and its derivatives in the solution. The positive values of ϕ_V (intercept)

and (slope) S_V decrease with the increase in temperature in all systems, supporting the view that urea and its derivatives cannot behave as structure makers in aqueous solution. The negative values of ϕ_K^0 (Tables 1–5) indicate electrostriction and hydrophobic interaction. The negative values of ϕ_K^0 are also attributed to the loss of structural compressibility of solvent molecules due to the increased population of four bonded water molecules, showing that the structural disruption is much more effective in water.

Urea may be regarded as alkaline in water, acting as a proton donor and acceptor and hence in a mixture of urea and water, the structure is likely to be broken [34]. Frank's theory [35] suggests that urea plays the role of a statistical structure breaker. The values of the viscosity interaction coefficients A and B are negative. These values increase markedly on lowering the temperature (Table 6). The negative values of viscosity coefficients A and B clearly indicate the structure-breaking behaviour of urea and its derivatives.

From the viscosity data, it should be possible to deduce the solute activation parameters. The values provide information about the macroscopic relaxation process; they increase with increasing temperature in all aqueous systems of urea and its derivatives. Since the values of thermodynamic parameters do not vary regularly with the rise in concentration of urea and its derivatives, the average values of these systems are presented in Table 8.

The apparent molal volume, apparent molal compressibility and other thermodynamic parameters (e.g. enthalpy, entropy and free energy of activation for viscous flow) are calculated using the measured values of ultrasonic velocity, density and viscosity. The apparent molal volumes, calculated from the density data listed in Tables 1–5, agree well with those from Masson's equation, as the plots of ϕ_V vs. \sqrt{C} are linear. It was observed that apparent molal volumes have positive values for all the systems which indicate solute–solvent interaction in the solutions. ϕ_V increases considerably with temperature for the aqueous solutions of thiourea, acetamide and tetramethylurea (Tables 2, 3, 5), while in urea + water and N, N' -dimethylurea + water systems, the positive values of ϕ_V show an increment at 30°C but further decrease with increasing temperature (Tables 1 and 5). The change in the values of ϕ_V with respect to temperature are very small so temperature-dependent apparent molal volumes do not supply exact information about the behaviour of urea and its derivatives. However, ϕ_V values for all the systems show a marked decrease with increasing solute concentration. Such behaviour indicates that solute–solvent interaction decreases with increasing concentration of urea and its derivatives. The positive values of ϕ_V (intercept) and S_V (slope) decrease with increasing temperature for all the systems, supporting the view that urea and its derivatives cannot behave as “structure makers” in aqueous solution.

The values of partial molal volume (ϕ_V^0) and partial molal compressibility (ϕ_K^0) are depicted in Table 5. The values of Gibbs free energy change ΔG^*

TABLE 1
 Apparent molal volume and apparent molal compressibility for the system urea + water at 25, 30, 35 and 40 °C

C (mol l ⁻¹)	25 °C		30 °C		35 °C		40 °C	
	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)
0.01	100.45	-8.54	100.66	-3.61	90.77	-0.06	90.99	-4.13
0.02	90.39	-11.52	90.57	-6.07	90.76	-4.09	90.88	-3.63
0.03	83.68	-18.70	83.84	-9.06	84.01	-5.74	84.21	-1.41
0.04	82.84	-26.47	82.99	-10.45	83.17	-6.45	83.36	-1.95
0.05	82.33	-37.99	82.49	-20.37	82.66	-12.75	82.85	-2.08
0.06	81.99	-33.11	82.15	-20.27	82.31	-15.77	82.51	-7.06
0.07	80.32	-31.12	80.47	-20.26	80.63	-15.55	80.82	-8.81
0.08	80.31	-31.09	80.46	-19.45	80.62	-15.23	80.81	-9.56
0.09	79.20	-31.20	79.45	-18.31	79.50	-15.21	79.68	-10.65

Uncertainty in the values of $\Delta\beta_s$, ϕ_v and $\phi_K \times 10^3$ is 0.1%.

TABLE 2

Apparent molal volumes and apparent molal compressibility for the system thiourea + water at 25, 30, 35 and 40 °C

C (mol l ⁻¹)	25 °C			30 °C			35 °C			40 °C		
	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)
0.01	106.50	-19.32	106.72	-8.37	106.92	-10.43	107.18	-3.43	107.18	-3.43	107.18	-3.43
0.02	101.47	-20.07	101.67	-8.60	101.85	-12.18	102.10	-3.15	102.10	-3.15	102.10	-3.15
0.03	99.79	-22.01	99.98	-10.37	100.16	-12.77	100.40	-2.73	100.40	-2.73	100.40	-2.73
0.04	98.95	-28.79	99.14	-11.26	96.79	-12.93	97.02	-4.15	97.02	-4.15	97.02	-4.15
0.05	98.44	-39.52	98.63	-20.89	96.79	-14.16	97.01	-4.91	97.01	-4.91	97.01	-4.91
0.06	98.10	-34.27	98.29	-20.59	96.78	-17.01	97.01	-6.27	97.01	-6.27	97.01	-6.27
0.07	96.43	-32.02	96.61	-20.30	95.30	-16.52	95.56	-9.18	95.56	-9.18	95.56	-9.18
0.08	96.42	-31.80	96.60	-19.53	94.25	-15.39	94.47	-8.86	94.47	-8.86	94.47	-8.86
0.09	95.31	-31.57	95.48	-18.19	93.41	-15.19	93.62	-10.63	93.62	-10.63	93.62	-10.63

Uncertainty in the values of $\Delta\beta$, ϕ_v and ϕ_K is 0.1%.

TABLE 3
 Apparent molal volume and apparent molal compressibility for the system of acetamide + water at 25, 30, 35 and 40 °C

C (mol l ⁻¹)	25 °C			30 °C			35 °C			40 °C		
	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)
0.01	109.51	-142.67	109.75	-83.65	120.69	-62.23	120.44	-38.17	120.44	-62.23	120.44	-38.17
0.02	94.42	-84.69	94.61	-43.63	99.86	-35.45	100.13	-26.47	100.13	-35.45	100.13	-26.47
0.03	89.39	-63.03	89.52	-35.67	93.12	-32.24	93.35	-24.26	93.35	-32.24	93.35	-24.26
0.04	86.87	-52.81	87.04	-33.21	89.74	-29.14	89.97	-22.91	89.97	-29.14	89.97	-22.91
0.05	85.36	-46.93	85.53	-30.53	87.71	-27.28	87.93	-22.51	87.93	-27.28	87.93	-22.51
0.06	84.35	-40.57	84.51	-28.75	86.36	-26.05	86.57	-21.92	86.57	-26.05	86.57	-21.92
0.07	82.19	-37.52	82.35	-26.53	83.95	-25.09	84.16	-21.41	84.16	-25.09	84.16	-21.41
0.08	81.83	-35.90	81.99	-25.07	83.41	-24.32	83.61	-21.24	83.61	-24.32	83.61	-21.24
0.09	80.43	-32.31	80.59	-23.76	81.16	-23.78	82.06	-20.93	82.06	-23.78	82.06	-20.93

Uncertainty in the values of $\Delta\beta_s$, ϕ_v and ϕ_κ is 0.1%.

TABLE 4

Apparent molal volume and apparent molal compressibility for the system of *N, N'*-dimethylurea + water at 25, 30, 35 and 40 °C

<i>C</i> (mol l ⁻¹)	25 °C		30 °C		35 °C		40 °C	
	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_K \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)
0.01	128.59	-66.53	148.99	-25.63	139.19	-15.07	119.26	-2.91
0.02	123.56	-42.71	138.89	-25.10	134.12	-14.32	114.18	-2.63
0.03	118.52	-40.98	135.51	-23.28	132.42	-14.07	112.48	-2.21
0.04	113.49	-38.23	126.27	-22.20	123.99	-12.52	109.09	-2.11
0.05	110.47	-36.79	120.73	-19.13	118.94	-11.39	107.07	-2.05
0.06	108.46	-32.82	117.03	-19.12	115.57	-10.81	105.71	-2.02
0.07	107.02	-29.98	114.39	-19.11	113.16	-9.97	104.74	-1.99
0.08	105.95	-27.86	112.41	-18.99	111.36	-9.75	104.02	-1.97
0.09	105.11	-25.54	110.87	-18.90	109.95	-9.48	103.45	-1.96

Uncertainty in the values of $\Delta\beta_s$, ϕ_v and ϕ_K is 0.1%.

TABLE 5
 Apparent molal volume and apparent molal compressibility for the system of tetramethylurea + water at 25, 30, 35 and 40 °C

C (mol l ⁻¹)	25 °C		30 °C		35 °C		40 °C	
	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)	ϕ_v (ml mol ⁻¹)	$\phi_\kappa \times 10^3$ (cm ³ mol ⁻¹ bar ⁻¹)
0.01	176.65	-6.14	177.01	-6.29	177.37	-2.32	177.82	-1.39
0.02	151.52	-6.28	151.79	-6.41	152.08	-4.45	152.44	-4.01
0.03	146.49	-8.54	146.75	-8.33	147.02	-7.04	147.35	-6.78
0.04	141.46	-9.54	141.71	-9.41	141.96	-8.46	142.28	-8.03
0.05	138.44	-7.72	138.68	-5.83	138.93	-5.67	139.23	-5.34
0.06	134.76	-3.56	134.98	-3.67	135.22	-2.87	135.50	-2.77
0.07	127.82	-1.49	128.03	-1.60	128.24	-0.92	128.51	-0.83
0.08	122.62	+0.82	122.81	0.72	123.01	1.19	123.25	1.39
0.09	119.69	3.34	119.87	1.90	120.06	3.55	120.19	3.62

Uncertainty in the value of $\Delta\beta_s$, ϕ_v and ϕ_κ is 0.1%.

TABLE 7
Viscosity interaction coefficients of Jones-Dole equation

System	25°C		30°C		35°C		40°C	
	Coefficient B	Coefficient A	Coefficient B	Coefficient A	Coefficient B	Coefficient A	Coefficient B	Coefficient A
Urea + water	-1.00	-1.02	-0.67	-1.01	-0.57	-1.00	-0.57	-0.98
Thiourea + water	-1.04	-1.03	-1.00	-1.00	-0.67	-0.98	-0.48	-0.98
Acetamide + water	-1.50	-1.16	-0.88	-0.91	-0.56	-0.90	-0.88	-0.89
<i>N, N'</i> -dimethyl urea + water	-2.35	-1.38	-1.36	-1.11	-0.62	-0.98	-0.40	-0.97
Tetramethyl-urea + water	-4.37	-1.56	-3.33	-1.29	-2.73	-1.17	-2.41	-1.11

TABLE 8
Average values of thermodynamic parameters for the system of urea and its derivatives at 25, 30, 35 and 40°C

System	25°C			30°C			35°C			40°C		
	ΔG^* (kcal)	ΔS^* (e.u.)	ΔH^* (kcal)	ΔG^* (kcal)	ΔS^* (e.u.)	ΔH^* (kcal)	ΔG^* (kcal)	ΔS^* (e.u.)	ΔH^* (kcal)	ΔG^* (kcal)	ΔS^* (e.u.)	ΔH^* (kcal)
Urea	15.47	15.49	4630.98	15.67	15.69	4769.12	15.88	15.88	4907.80	16.06	16.08	5049.29
+ water												
Thiourea	15.48	15.58	4634.19	15.68	15.69	4769.39	15.87	15.89	4909.96	16.08	16.09	5052.88
+ water												
Acetamide	15.48	15.49	4633.50	15.66	15.67	4764.14	15.86	15.87	4904.12	16.06	16.07	5046.37
+ water												
<i>N, N'</i> -												
Dimethyl urea	15.51	15.52	4642.23	15.69	15.70	4774.45	15.88	15.90	4912.67	16.08	16.10	5055.63
+ water												
Tetramethyl urea												
+ water	15.52	15.53	4645.66	15.70	15.71	4777.05	15.89	15.91	4915.25	16.09	16.10	5057.46

can be interpreted on the basis of stability of urea and its derivatives in water and depend on the extent of hydrogen bonding. Hydrogen bonding occurs between the alkyl group of the solute molecules of urea and water molecules. The structure-breaking behaviour of urea and its derivatives causes the slight variation in ΔG^* values. Values of other activation parameters, ΔS^* and ΔH^* , also support this suggestion. The values of thermodynamic parameters of activation for the viscous flow, viz. ΔG^* , ΔS^* and ΔH^* , clearly indicate a macroscopic relaxation process. The values of ΔG^* , ΔS^* and ΔH^* indicate that these parameters are greatly influenced by temperature, increasing positively with increasing temperature.

Barone et al. [36] have also pointed out from a spectroscopic study that the structure-forming ability of tetramethylurea in liquid water is stronger than that of *N, N'*-dimethylurea. The variation in the values is thus attributed to the behaviour of methyl groups in water. The methyl group of urea and its derivatives seems to rotate almost without steric hindrance in water. Thus, the tetramethylurea–water interaction is found to be essentially similar to that of *N, N'*-dimethylurea solution at low concentrations. Tetramethylurea [37] acts only as a hydrogen bond acceptor, since all atoms of hydrogen of the amide nitrogen are substituted by the $-\text{CH}_3$ group. Thus, it is tentatively assumed that tetramethylurea is formed in aqueous solution by hydrogen bonding.

Thus, we can conclude that urea and its derivatives, viz. thiourea, acetamide, *N, N'*-dimethylurea and tetramethylurea, play the role of structure breaker in water. The study also indicates the influence of temperature on the ultrasonic and thermodynamic parameters. Alkyl groups of urea and its derivatives take part in the solute–solvent interaction, which decreases with the increasing solute concentration. The interaction also decreased with rising temperature. Such behaviour of urea and its derivatives is observed in aqueous systems, but it may be different in non-aqueous solutions. The study of urea and its derivatives in non-aqueous solutions is in progress and will be communicated separately.

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