

EXPERIMENTS FOR HYDROPHILIC AND HYDROPHOBIC INTERACTIONS ANALYSIS OF N-METHYL UREAS WITH WATER USING DENSITY AND SURFACE TENSION

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Abstract. Surface tension ($\gamma \pm \text{mNm}^{-1}$) of urea, 1-methylurea (MU), 1, 3-dimethylurea (DMU) and 1,1,3,3-tetramethylurea (TMU) as N, N'-ureas were obtained at 7.99 to 7.01 pH and 293.15, 298.15 and 303.15 K temperatures for 0.005 to 0.25 mol kg⁻¹ at an interval of 0.005 mol kg⁻¹ solutions. Limiting surface tension γ^0 data were obtained from regression analysis. The contributions of -CH₃ (methyl) groups were analyzed from a difference of the γ^0 values of consecutive ureas. The γ^0 data illustrated weakening of hydrophilic and strengthening of hydrophobic interactions with each -CH₃ group and inferred a shift from hydrophilic-hydrophilic to hydrophilic-hydrophobic interactions. The γ^0 data illustrated a structure making action of the TMU.

Keywords: hydrophobic, hydrophilic, tetramethylurea, interactions, structure breaking

Introduction

The N, N' Ureas with water are effective mixed solvents for protein chemistry and biological processes. Their interactions elucidate intermolecular forces responsible for biological processes. The cohesive forces [1] of mixed solvents are due to hydrophilic and hydrophobic interactions [2] with variable polarity [3, 4] and define a stability of proteins, nucleic acids and membrane to focus a cage approach of the

solvents for biomolecules like sarcosylsarcosine [5]. A number of studies on ureas with different probes are reported [6, 7] but the surface tensions are yet to be reported [8-13]. The H substitution of the amino group ($-\text{NH}_2$) by the $-\text{CH}_3$, enhanced hydrophobic interactions. It weakened hydrogen bonding of substituted $-\text{NH}_2$ and also weak hydrogen bonding of carbonyl group ($>\text{C}=\text{O}$) [14]. So ureas denature the biopolymers [15-18]. At low temperature Stokes studied [19] the structural interactions with urea and alkyl derivatives and noted as structure breaker [20-25]. A long-range arrangement of electrostatic forces of water with higher dipole moment influences the hydrophilic and hydrophobic interactions with polar and non-polar compounds like urea and tetramethylurea. The urea, dimethylurea, 1,3-dimethyl carbamate, diethyl ether, methyl acetate and ethyl alcohol were used with polyurethane for hydrogen bond length, energy and IR spectra [25, 26]. A small angle neutron scattering, NMR relaxation and self-diffusion coefficient studies on aqueous TMU showed a hydrophobic interaction. Many models like lattice and statistical, mechanical, osmotic and activity coefficient of N, N' ureas [27] furnish better understanding of hydrophobic interactions of mono-, di-, and tetra- substituted molecules.

Experiment

The solutions, w/w, were prepared with Millipore water having $1.10^{-6} \Omega^{-1}\text{cm}^{-1}$ conductivity, (urea, methylurea, dimethylurea and tetramethylurea, AR, Merck), were dried for 24 h keeping over night in a vacuum dessiccator and stored in P_2O_5 filled desiccator. The tetramethylurea (Merck Schuchardt) is a high boiling point liquid (BP, 449.65 K) and was used as received. The densities were determined with weight method using bicapillary pycnometer at a fairly constant temperature [2]. The weighing was made with 0.01mg analytical Dhona balance, model 100 DS, Instruments Pvt Ltd, Calcutta, India. The surface tensions were measured with Survismeter [19] at $\pm 0.01^\circ\text{C}$ temperature control, read with Beckman thermometer.

Result

The densities values were calculated as usual [2] and the density of water is taken from literature [28]. The surface tensions (γ) were calculated usual relation [4], the data are regressed and constants are given in Table 1 and difference in data in Table 2.

Table 1. Regression constants of the ρ and γ data and slopes for systems

Systems	Density constants		Surface tension constants	
	ρ^0 10^3 kg m^{-3}	S_d $10^3 \text{ kg}^2 \text{ m}^{-3} \text{ mol}^{-1}$	γ^0 mN m^{-1}	S_s $10^{-2} \text{ m N m}^{-1} \text{ mol}^{-1}$
			293.15 K	
U	0.99831	0.0104	72.76	0.75
MU	0.99832	0.0079	71.86	17.74
DMU	0.99821	0.0079	73.61	9.22
TMU	0.99822	0.0075	78.01	-24.74
			298.15 K	
U	0.99712	0.0101	71.96	0.73
MU	0.99713	0.0077	71.01	-1.94
DMU	0.99682	0.0072	72.73	12.20
TMU	0.99651	0.0068	77.12	43.30
			303.15 K	
U	0.99574	0.0100	71.16	-0.65
MU	0.99542	0.0079	69.88	5.10
DMU	0.99562	0.0053	72.14	-2.13
TMU	0.99551	0.0048	77.94	-25.35

Table 2. Contribution of methyl group calculated from ((N-ureas)-(urea))/n, n denotes-CH₃ groups numbers

For ρ^0						
Temp., K	MU-U	DMU-U	TMU-U	DMU-MU	TMU-MU	TMU-DMU
293.15	0.00000	-0.00005	-0.00003	-0.00010	-0.00003	0.00000
298.15	0.00000	-0.00015	-0.00015	-0.00030	-0.00020	-0.00015
303.15	-0.00030	-0.00005	-0.00005	0.00020	-0.00003	-0.00005
For γ^0						
293.15	-0.90	0.42	1.31	1.75	2.05	2.20
298.15	-0.95	0.38	1.29	1.72	2.03	2.19
303.15	-1.28	0.49	1.69	2.26	2.68	2.90

Discussion

The ρ^0 values with each -CH₃ groups are as U = MU > DMU = TMU, U = MU > DMU > TMU, U > DMU > TMU > MU for 293.15, 298.15 and 303.15 K (Table1), respectively, with sequential strength of intermolecular forces. The ρ^0 va-

lues for urea are higher than those of the others with stronger hydrophilic interactions with stronger intermolecular forces than those of others. The urea with both the amino ($-\text{NH}_2$) and ketonic ($>\text{C}=\text{O}$) groups strongly disrupts the hydrogen bonded water structure and develops stronger hydrogen bonded structure than the water. The hydrogen bonding centers of the urea are $2(-\text{H}-\text{N}-\text{H}-) + 2(-\text{H}-\text{N}-\text{H}-) + 1 (>\text{C}-\text{O}-) = 5$ and hence the 5 times hydrophilic (philic): 0 times hydrophobic (phobic) interactions are noted. The ρ^0 values at 293.15 and 298.15 K for MU are lower than those of the urea with comparatively weaker intermolecular forces. The $-\text{CH}_3$ of MU weaken hydrophilic strengthen hydrophobic interaction in same proportion, and at 303.15 K, the interactions weakest. The 4(philic):1(phobic) ratio is noted with the MU against the 5(philic): 0(philic) of the U. Similarly the ratios are as 3(philic): 2(phobic) and 0(philic): 5(phobic) for DMU and TMU, respectively. So with DMU and TMU the hydrophobic interactions dominate over the hydrophilic and the water developed a cage around the $-\text{CH}_3$ groups. The decrease in the ρ^0 values with the $-\text{CH}_3$ infer weaker intermolecular forces with mild disruption in structure as compared to U. Hence the $-\text{CH}_3$ weakens the structure breaking and strengthen making strengths as compare to U (Table 2). The ρ^0 values of the DMU at 303.15 K predict micelles formation and bursting and a decrease in the ρ^0 values with temperatures infers destabilization solute-solvent interactions. The S_d values are as $U > MU > DMU > TMU$, and the compositions strongly influence the hydrophilic interactions as compared to the hydrophobic. The U with composition develops stronger dipolar interactions which weaken as $MU > DMU > TMU$. A structure breaking effect of N-ureas decreases and the making increases. The $-\text{CH}_3$ weakens the disruption mechanism favoring a cage formation. The lowest S_d values for TMU infer weaker hydrophobic interactions.

The γ^0 data (Table1) are as $TMU > DMU > U > MU$, with higher cohesive forces with TMU due to purely hydrophobic interactions. It developed higher integrated molecular forces with stronger adhesion on the glass capillary. The $-\text{CH}_3$ with the N^+ and $>\text{CO}^-$ developed stronger intermolecular forces with higher surface forces. The γ^0 values of MU decrease because of an asymmetric structure that disbalances the surface forces and the γ^0 values for DMU and TMU are noted higher due to symmetric structure. The U and MU with comparatively stronger hydrophilic interactions produce the lower γ^0 values with weaker surface forces (Tables 1 and 2).

The S_s data are as $293.15 > 298.15 > 303.15$ for U; the $293.15 > 303.15 > 298.15$ for MU and the $298.15 > 293.15 > 303.15$ for both the DMU and TMU. The temperature affects surface forces. The U induces stronger structure breaking at 293.15 K than that of 298.15 and 303.15 while the MU stronger breaking at 293.15 K than those of the 303.15 and 298.15 K. The DMU and TMU induce similar structure breaking actions however comparatively at 298.15 K they show stronger breaking actions than those of the 293.15 and 303.15 K. The γ^0 and slope values (Table 1) mark $-\text{CH}_3$ responsible for introducing an element of the structure making [22, 24]. The transition

point in the values with compositions infers the micelle formation, which has similar information of Barone [29]. The differences in values of the γ^0 (Table 2) for consecutive N-ureas derive the contribution of the $-\text{CH}_3$ and perhaps the size of molecule, composition of solution, temperature does influence the extent of solvation of N-ureas.

An increment in the γ^0 data with the $-\text{CH}_3$ is due to structured solutions and the γ^0 is because of $\gamma^0 = (\gamma_{\text{vw}} + \gamma_{\text{v}}) + (\gamma_{\text{s}} + \gamma_{\text{h}})$ factors. The γ_{vw} is due to van der Waals force, the γ_{v} void spaces. The γ_{s} is from solute-solvent interactions, and γ_{h} hydrophobic hydration. The $(\gamma_{\text{vw}} + \gamma_{\text{v}})$ values for U is almost same and hence a variation in the $(\gamma_{\text{s}} + \gamma_{\text{h}})$ explain the γ^0 and $(\gamma_{\text{s}} + \gamma_{\text{h}})$ values for U and N-ureas and are depicted as $(\gamma_{\text{vw}} + \gamma_{\text{v}})_{\text{w}} = \gamma_{\text{uw}} + \gamma_{\text{ww}}$ and $(\gamma_{\text{s}} + \gamma_{\text{h}})_{\text{w+s}} = \gamma_{\text{uw}} + \gamma_{\text{uu}} + \gamma_{\text{ww}}$. Here the γ_{uw} , γ_{uu} ($_{\text{u}}$ indicates N-ureas) and γ_{ww} are the contributions from the N-ureas-water, N-ureas-N-ureas and water-water interaction, respectively where $\gamma^0 = \gamma_{\text{uw}} + \gamma_{\text{uu}} + \gamma_{\text{ww}}$. So a slight decrease in γ^0 with temperature is contributed from the γ_{uw} values due to electrostricted regions of the $>\text{CO}^-$ and NH_2^+ ions. The changes in the γ_{ww} values are relatively smaller and the S_{s} values for the N-ureas are as $\text{MU} > \text{U} > \text{DMU} > \text{TMU}$ at 293.15 and 298.15 $\text{U} > \text{DMU} > \text{TMU} > \text{MU}$ at 303.15 K. The positive S_{s} values of U infer stronger structure breaking with compositions and the negative values explain weaker solute-solvent interaction. The DMU and TMU have negative S_{s} values and behave weaker structure breakers. The MU at 293.15 and 298.15 has positive values and at 303.15 K, the negative due to structure breaking and making with respect to temperature.

The S_{s} values decrease at 303.15 K as the urea disrupts water structure making it a free liquid. The S_{s} values with U are as 298.15 > 293.15 > 303.15; MU as 293.15 > 298.15 > 303.15; DMU as 293.15 > 298.15 > 303.15 and TMU as 293.15 > 303.15 > 298.15 having similar influence of temperature on hydrogen bond disruption as of compositions. For urea at 298.15 K, the structure breaking action is stronger than that of the 293.15 and 303.15 K while DMU and TMU show similar action of structure breaking however the TMU causes stronger breaking action with compositions and the weaker at 298.15 K. The S_{s} values for TMU infer that the $-\text{CH}_3$ vigorously reorients the bulk water for cage formation at 293.15 K than that of the 303.15 and 298.15 K.

Conclusion

The hydrophobic interaction develops stronger cohesive forces with an effective caging around the N-ureas with each $-\text{CH}_3$. The densities decrease and the γ^0 values increase with temperature with similar trends.

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REFERENCES

1. **Singh, M., S. Kumar.** Viscometric Studies of Poly (N-vinyl -2-pyrrolidone) in water and in water and 0.01% Bovine serum albumin at 283.15, 288.15, 293.15, 298.15, 303.15, 308.15 and 313.15 K. *J. Appl. Polym. Sci.* **87**, 1001-1015 (2003).
2. **Singh, M., H. Chand, K.C. Gupta.** Density and Viscosity of Bovine Serum Albumin Egg Albumin and Lysozyme in Aqueous and RbI, CsI and DTAB Aqueous Solutions at 303.15 K and Molecular Interactions. *Chemistry & Biodiversity* **2**, 809-824 (2005).
3. **Singh, M.** Simultaneously Study of Interfacial Tension, Surface Tension and Viscosity of few Surfactants Solutions with Survismeter, *Surface & Interface Analysis* **40**, 1344-1349 (2008).
4. **Singh, M.** Survismeter-type 1 and 2 for Surface Tension and Viscosity Measurements of Liquids for Academic, Research and Development Studies. *J. Biochem. Biophys. Methods*, **67**, 151-161 (2006).
5. **Castronuovo, G., R.P. Dairo, C. Della Volpe, V. Elia.** A Model for the Interaction between Hydrophilic and Hydrophobic Solutes-Aqueous Solutions Containing Biuret or Urea and Hydroxylated Substances. *Thermochimica Acta* **206**, 43-54 (1992).
6. **Cristinziano, P., F. Lelj, P. Amodeo, G. Barone, V. Barone.** Stability and Structure of Formamiae and Urea Dimers in Aqueous Solutions, A Theoretical Study. *JCS Faraday Trans.1* **85**, 621-632 (1989).
7. **Yilgor, E., E. Yurtsever, I. Yilgor.** Hydrogen Bonding and Polyurethane Morphology. II. Spectroscopic, Thermal and Crystallization Behavior of Polyether Blends with 1, 3-dimethylurea and a Model Urethane Compound. *J. Polymer* **43**, 6561-6568 (2002).
8. **Yilgor, I., T.C. Ward, E. Yilgor, G.E. Attila.** Anomalous Dilute Solution Properties of Segmented Polydimethylsiloxane-Polyurea Copolymers in Isopropyl Alcohol. *Polymer* **46**, 1179-1186 (2006).
9. **Costantino, L., G.D. Errico, P. Roscigno, V. Vitagliano.** Effect of Urea and Alkylureas on Micelle Formation by a Nonionic Surfactant with Short Hydrophobic Tail at 250C, *J. Phys. Chem. B* **104**, 7326-7333 (2000).
10. **Jones, M.N.** *Biochemical Thermodynamics*, Elsevier, New York, 1979, Chap. 2.
11. **Franks, F.** *Water: A Comprehensive Treatise*. Plenum Press, New York, 1978.
12. **Neurath, H.** *The Proteins*. Academic Press, New York, 1974
13. **Cobos, E.S., V.V. Filimonov, A. Galvez, E. Valdivia, M. Maqueda, J.C. Martinez, P. L. Mateo.** The Denaturation of Circular Enterocin AS-48 by Urea and Guanidinium Hydrochloride. *Biochim. Biophys. Acta* **1598**, 98-107 (2002).
14. **Singh, M., S. Gupta.** Synthesis, Molecular Weights, Viscometric and Structural Studies of 1st and 2nd Tier Generation Melamine Based Dendrimers. *Synthetic Commn.* **38**, 898-2907 (2008).
15. **Singh, M., Y.K. Sharma.** Activation Energy and Transition State Theory Applications for Interactions of Nucleos (t)ides and Furanose Puckering in Aqueous Medium from 288.15 to 298.15 K. *Physics & Chemistry of Liquids* **44**, 1-14 (2006).

- 16. Franks, F., J.E. Desnoyers.** Water-Alcohol Mixtures Revisited (pp. 171-232). In.: Franks, F. (Ed.). *Water Science Reviews 1*. Cambridge University Press, Cambridge, 1985.
- 17. Modig, K., E. Kurian, F.G. Prendergast, B. Halle.** Water and Urea Interactions with the Native and Unfolded Forms of a β -barrel. *Protein Science* **12**, 2768-2781 (2003).
- 18. Singh, M.** Preparation and Structural Characterization of Melamine- Methylurea-Formaldehyde Resin and Its Blends Separately with Ethyl Cellulose, Starch, Teakwood and Almond Shell Powders by C13NMR, IR, TGA and SEM Techniques. *J. Appl. Polym. Sci.* **92**, 3437-3446 (2004).
- 19. Singh, M.** A Simple Instrument for Measuring the Surface Tension and Viscosity of Liquids. *J. Instr. Exp. Tech*, **48**, 270-271 (2005).
- 20. Apelblat, A., E. Manzurola.** Volumetric Properties of Water and Solutions of Sodium Chloride and Potassium Chloride at Temperatures from T = 277.15 K to T = 343.15 K at Molalities of (0.1, 0.5, and 1.0) mol kg⁻¹. *J. Chem. Therm.* **31**, 869-893 (1999).
- 21. Nelson, D.L., M.M. Cox.** *Lehninger Principles of Biochemistry*. Macmillan, New York, 2000.
- 22. Singh, M.** Studies of Intermolecular Force Coefficient (σ_{im}^0) for Methyl Derivatives of Urea in Aqueous Solutions with Friccohesity, A New Physicochemical Function, from 293.15 to 303.15 K, *J. Ind. Chem. Soc.* **82**, 1183-1189 (2005).
- 23. Singh, M., M. Pandey.** Excess Viscosities (η^E) of Glycine with Halide Salts of Alkali Metals of IA Group in Aqueous Solutions at 310.15 K for Structural Interactions. *J. Ind. Chem. Soc.* **82**, 1091-1102 (2005).
- 24. Singh, M., A. Kumar.** Hydrophobic Interactions of N-Methylureas in Aqueous Solutions Estimation from Density, Molal Volume, Viscosity and Surface tension. *J. Solution Chemistry* **35**, 567-582 (2006).
- 25. Lubert, S.** *Biochemistry*. W.H. Freeman, New York, 1995.
- 26. Singh, M., S. Kumar.** Activation Energy, Free Energy, Enthalpy and Entropy Changes Associated with Viscometric Changes of Extremely to Moderately Dilute Aqueous Solutions of Polyvinylpyrrolidone at 288.15-313.15 K. *J. Appl. Polym. Sci.* **93**, 47-55 (2004).
- 27. Singh, M.** Studies of Molecular Interactions of α -amino Acids in Aqueous and Cationic Surfactants Systems Investigated from Density and Apparent Molal Volume at 283.15, 288.15 and 293.15 K. *Pakistan J. Sci. Res.* **48**, 303-311 (2005).

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