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

Man SINGH
University of Delhi, INDIA

Abstract. Surface tension ($\gamma \pm mNm^{-1}$) 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 $-CH_3$ (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 $-CH_3$ 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 (-NH_2) by the -CH_3, enhanced hydrophobic interactions. It weakened hydrogen bonding of substituted -NH_2 and also weak hydrogen bonding of carbonyl group (>C=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 polyurethene 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} $\Omega^{-1}cm^{-1}$ 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 pyknometer 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 $\pm$ 0.01^0C 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

	Density constants		Surface tension constants	
Systems	ρ^0 10^3 kg m^{-3}	S_d 10^3kg^{2}m^{-3}mol^{-1}	γ^0 mN m^{-1}	S_s 10^{-2} m N m^{-1}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-CH_3 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 -CH_3 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 ($-NH_2$) and ketonic (>C=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(--H-N-H--) +2(--H-N-H--) +1 (>C-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 $-CH_3$ 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 $-CH_3$ groups. The decrease in the ρ^0 values with the $-CH_3$ infer weaker intermolecular forces with mild disruption in structure as compared to U. Hence the $-CH_3$ 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 $-CH_3$ 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 $-CH_3$ with the N^+ and $>CO^-$ 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 $-CH_3$ 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 -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 -CH_3 is due to structured solutions and the γ^0 is because of $\gamma^0 = (\gamma_{vw} + \gamma_v) + (\gamma_s + \gamma_h)$ 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 V_h hydrophobic hydration. The $(\gamma_{vw} + \gamma_v)$ values for U is almost same and hence a variation in the $(\gamma_s + \gamma_h)$ explain the γ^0 and $(\gamma_s + \gamma_h)$ values for U and N-ureas and are depicted as $(\gamma_{vw} + \gamma_v)_w = \gamma_{uw} + \gamma_{ww}$ and $(\gamma_s + \gamma_h)_{w+s} = \gamma_{uw} + \gamma_{uu} + \gamma_{ww}$. Here the γ_{uw}, γ_{uu} ($_u$ indicates N-ureas) and γ_{ww} are the contributions from the N-ureas-water, N-ureas-N-ureas and water-water interaction, respectively where $\gamma^0 = \gamma_{uw} + \gamma_{uu} + \gamma_{ww}$. So a slight decrease in γ^0 with temperature is contributed from the γ_{uw} values due to electrostrictied regions of the $>CO^-$ 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 MU > U > DMU > TMU at 293.15 and 298.15 U > DMU > TMU > 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 -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 -CH_3. The densities decrease and the γ^0 values increase with temperature with similar trends.

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✉ **Dr. Man Singh**,
Chemistry Research Laboratory,
Deshbandhu College,
University of Delhi,
New Delhi 110019, INDIA
E-Mail: mansingh50@hotmail.com