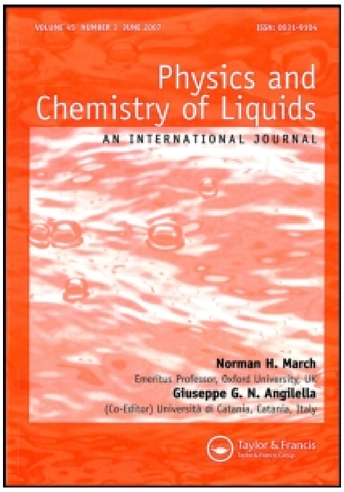

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Volumetric and Viscometric Studies on an Aqueous Urea Solution

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VOLUMETRIC AND VISCOMETRIC STUDIES ON AN AQUEOUS UREA SOLUTION

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Of late there has been a renewed inerest in the thermodynamics and other investigations on the behaviour of urea (denaturants) in aqueous solution which induce changes in structure and properties of proteins including their solubility, denaturation, dissociation into subunits and the activity of enzymes. With this in view, density and viscosity of aqueous urea solutions were determined as a function of concentration at 35, 40, 45, 50 and 55°C, respectively. The apparent molal volume (ϕ_v) of urea was found to be linear function of solute concentration. From the ϕ_v *versus* molality (m) plot the apparent molal volume at infinite dilution, ϕ_v^o (taken to be equal to partial molal volume, $\bar{V}_2^o$) was determined. Viscosity coefficients B and D were calculated on the basis of the viscosity of the solutions and the solvent concerned using the Jones–Dole equation. The activation parameters for viscous flow ($\Delta G^{\neq}$, $\Delta S^{\neq}$ and $\Delta H^{\neq}$) were also calculated by means of the Eyring equation. The data were interpreted in terms of the structure making behaviour of urea in water at 35–55°C temperature range.

Keywords: Apparent and partial molal volumes; Viscosity coefficient;
Activation parameter

INTRODUCTION

The volumetric, viscometric and other thermodynamic data provide valuable information regarding solute–solvent, solute–solute and solvent–solvent interactions [1,2]. The structure of urea–water mixtures is of considerable importance in understanding protein

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denaturation [3,4]. A large number of researchers [5–11] reported that urea acts as a net structure breaker for water. Abu-Hamidayyah [12], on the other hand, reported that urea enhances water structure. This latter view has been severely criticized by Holtzer and Emerson [13]. A third possible view based on thermochemical and nmr studies is that urea has essentially no net effect on water structure [14]. Thus the behaviour of urea on water structure is conflicting and the nature of urea-water interaction is not yet clearly understood.

Considering these matters we therefore desire to study the aqueous urea system in different conditions to see whether urea has no net effect on water structure or urea enhances water structure or the more popular view that urea tends to break the water structure.

EXPERIMENTAL

Urea (99%) was procured from E. MERCK. The chemicals with quoted purities were dried at room temperature in vacuum over phosphorus pentoxide for at least 24 h and were used without further purification. The water used for solution were doubly distilled. The density were measured by using a 10 ml bicapillary pycnometer calibrated previously with water. The viscosity were measured by calibrated U-type Ostwald viscometer of the British standard institution with sufficiently long efflux time to avoid kinetic energy correction. The time of flow was recorded by a timer capable to read up to ± 0.01 s. A METTLER PM-200 electronic balance with an accuracy of ± 0.0001 g was used for weighing. The temperature was controlled by a thermostatic water bath fluctuating to ± 0.1°C.

RESULTS AND DISCUSSION

The apparent molal volume (ϕ_v) of the urea–water system at different concentrations and temperatures estimated from the density data is recorded in Table I. Figure 1 shows the variation of the apparent molal volume (ϕ_v) with concentration and temperature. The figure shows that apparent molal volume (ϕ_v) varies linearly with molality

TABLE I Densities, viscosities, apparent molal volume and partial molal volume of urea in aqueous solutions at 35, 40 45, 50 and 55°C, respectively

Concen tration m (mol kg^{-1})	*Temper- ature* (°C)	*Density* (g cm^{-3})	*Apparent molal volume of urea, ϕ_v* (cm^3 mol^{-1})	*Partial molal volume of urea, $\bar{v}_2$* (cm^3 mol^{-1})	*Partial molal volume of urea at infinite dilution $\bar{v}_2^\circ$* (cm^3 mole^{-1})	*Partial molal volume of water $\bar{v}_1$* (cm^3 mol^{-1})	*Viscosity* η (cP)
1.0000	35	1.0086	45.0128	45.0643	44.9980	18.1067	0.7612
	40	1.0068	45.1168	45.1824	45.1001	18.1396	0.6912
	45	1.0047	45.4298	45.4810	45.4177	18.1763	0.6293
	50	1.0023	45.6097	45.6746	45.5600	18.2161	0.5841
	55	0.9997	45.9553	45.9928	45.9180	18.2599	0.5318
2.0008	35	1.0219	45.0821	45.1851	–	18.1039	0.7944
	40	1.0199	45.2020	45.3332	–	18.1361	0.7169
	45	1.0175	45.5153	45.6176	–	18.1735	0.6557
	50	1.0152	45.6611	45.7908	–	18.2126	0.6023
	55	1.0123	46.0001	46.0752	–	18.2579	0.5616
3.0000	35	1.0339	45.1585	45.3429	–	18.0993	0.8302
	40	1.0318	45.3172	45.5139	–	18.1302	0.7568
	45	1.0293	45.5717	45.7252	–	18.1689	0.6939
	50	1.0269	45.7327	45.9272	–	18.2068	0.6485
	55	1.0239	46.0363	46.1489	–	18.2545	0.5884
4.0007	35	1.0450	45.2296	45.4355	–	18.0928	0.8754
	40	1.0427	45.3983	45.6607	–	18.1219	0.7895
	45	1.0401	45.6494	45.8540	–	18.1625	0.7263
	50	1.0375	45.8357	46.0951	–	18.1986	0.6694
	55	1.0347	46.0562	46.2064	–	18.2498	0.6128
5.0000	35	1.0551	45.2968	45.5541	–	18.0844	0.9160
	40	1.0528	45.3983	45.7773	–	18.1113	0.8365
	45	1.0501	45.6494	45.9403	–	18.1542	0.7712
	50	1.0473	45.8357	46.2323	–	18.1881	0.7012
	55	1.0445	46.0562	46.2738	–	18.2437	0.6472
5.9999	35	1.0645	45.3342	45.6429	–	18.0742	0.9544
	40	1.0619	45.5442	45.9377	–	18.0983	0.8702
	45	1.0591	45.7572	46.0641	–	18.1440	0.7978
	50	1.0560	46.0198	46.4088	–	18.1753	0.7261
	55	1.0534	46.1592	46.3844	–	18.2363	0.6803
7.0002	35	1.0732	45.3727	45.7329	–	18.0622	1.0204
	40	1.0704	45.5972	46.0563	–	18.0829	0.9140
	45	1.0676	45.7997	46.1578	–	18.1320	0.8423
	50	1.0644	46.0564	46.5103	–	18.1601	0.7788
	55	1.0618	46.1890	46.4517	–	18.2275	0.7100
8.0004	35	1.0812	45.4128	45.8045	–	18.0483	1.0488
	40	1.0784	45.6355	46.1302	–	18.0652	0.9479
	45	1.0755	45.8429	46.2521	–	18.1182	0.8735
	50	1.0724	46.0574	46.5761	–	18.1452	0.8030
	55	1.0696	46.2099	46.5102	–	18.2173	0.7390
8.9999	35	1.0886	45.4583	45.8814	–	18.0325	1.0773
	40	1.0857	45.6741	46.2116	–	18.0451	0.9819
	45	1.0827	45.8941	46.2708	–	18.1026	0.9047
	50	1.0797	46.0771	46.6606	–	18.1227	0.8273
	55	1.0767	46.2588	46.5966	–	18.2058	0.7679

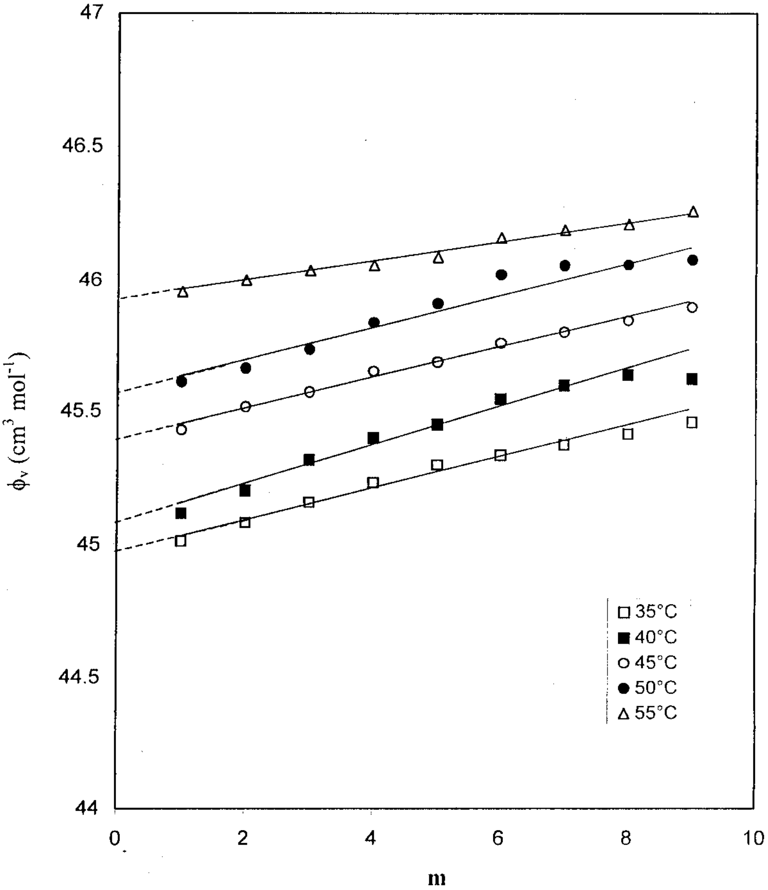

FIGURE 1 Plots of apparent molal volumes (ϕ_v) *versus* molality (m) for urea in aqueous solutions at 35, 40, 45, 50 and 55°C, respectively.

(m). Similar behaviour is also seen in case of temperature i.e. with rise of temperature the ϕ_v increases in the temperature range 35–55°C.

The partial molal volume of urea ($\bar{V}_2$) increases with the increase in molality but the partial molal volume of water ($\bar{V}_1$) slightly decreases with the increase in molality suggesting that solute–solvent interactions increase with the increase in molality of urea. The ϕ_v^o values which is also the partial molal volume of the solute at infinite dilution, $\bar{V}_2^o$ reflects the true volume of the solute and the volume change arising from the solute–solvent interactions, increases with the increase in temperature. This behaviour of ϕ_v^o with the increase in temperature may be due to the result of the following effects:

(i) at higher temperature the thermal energy of the water molecules is increased causing fast relaxation of the bulk electrostricted water molecules from the interaction regions of –NH$_2$ and –CO groups of urea and thereby resulting a positive volume change;
(ii) an increase in temperature render the urea–urea interaction relatively weaker giving rise to a small negative volume change; and
(iii) the water–water interactions decreases with the increase in temperature giving a very small negative change in volume.

The linear increase of ϕ_v with molality indicates that urea–water interactions increases with the increase in molality of urea at the experimental temperatures. Similar behaviour was reported previously by concentration dependence studies of apparent molal volume of aqueous urea solutions by Stokes [15]. He reported that at a temperature higher than 25°C, ϕ_v increases in a linear fashion, but at a low temperature (0°C), the ϕ_v change with concentration is little and that too in a nonlinear fashion. The linear increase of ϕ_v with the concentration of urea were also reported by Gucker *et al.* [16] in their density and apparent molal volume study of aqueous urea solutions at 25–30°C, respectively.

Viscosity of the aqueous urea solutions (1–9 m) were determined at 35, 40, 45, 50 and 55°C, respectively. The relevant data were shown in Table I and the results were represented graphically in Fig. 2. The viscosity *versus* molality plots for the above systems at different temperatures are linear. The value of η increases with the increase in molality of urea but decreases with the increase in temperature in all cases. According to the 'flickering cluster' model [17] water has large void spaces within the hydrogen-bonded framework of its structure. The linear increase of η with concentration may be interpreted by the fact that urea molecules penetrate in the void spaces of the hydrogen bonded framework of water and may have positive interaction with the solvent. The interactions seems to be strong. Thus urea may be considered as water structure maker at the temperature range of 35–55°C. Structure making property of urea has also been reported previously by Abu-Hamidayyah [12]. The structure making concept is reasonable on

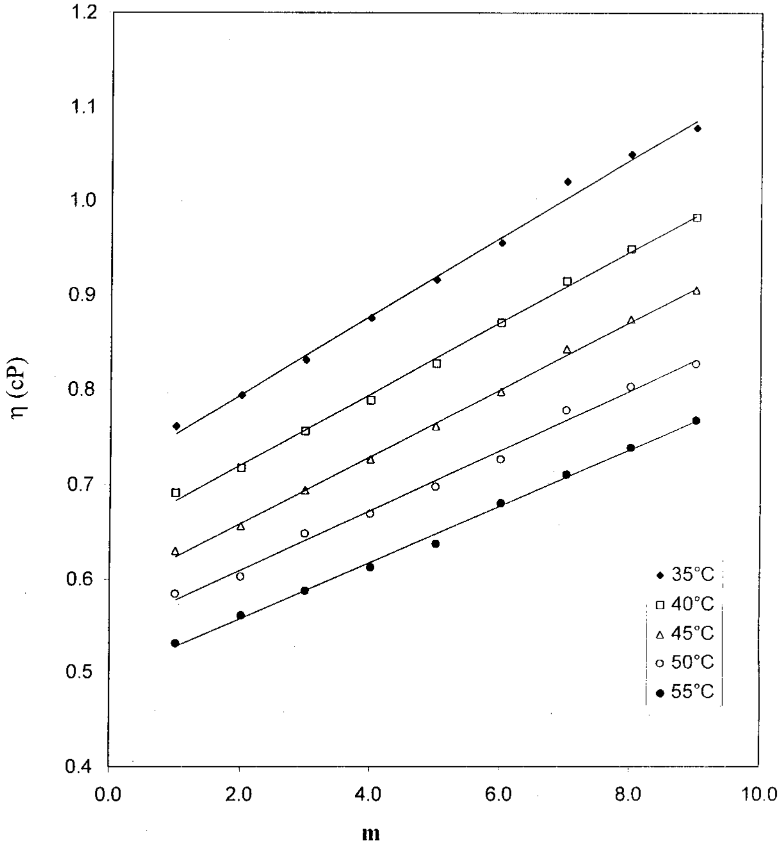

FIGURE 2 Plots of viscosity (η) *versus* molality (m) for urea in aqueous solutions at 35, 40, 45, 50 and 55°C, respectively.

the grounds that urea may enter into cluster formation in aqueous solutions due to its available hydrogen bonding groups –CO and –NH_2. Frank *et al.* [17] suggested that these groups in urea are able to enter clusters with only slight distortion, and to transmit both 'cluster-forming' and 'cluster-disrupting' tendencies, thereby modifying the water structure slightly.

If the hydrogen bonding in aqueous urea solutions are fundamentally different from those existing in pure water, i.e. if water molecules hydrogen bonded to urea are not able to hydrogen bond with other neighbouring molecules, then this should be reflected in the value of

B-coefficient in the Jones–Dole equation [18]. If the B-coefficient for urea in water is a positive quantity, it indicates a structure forming tendency and the value should be comparable to the corresponding values of structure-forming ions in water [19]. If the urea molecules tend to destroy water structure and produce disorder, then the B-coefficient value would be a negative quantity. The B-coefficient values obtained here (see Table II) strongly supports the former view. Although the B-coefficient data is usually reported to be effective in dilute solution [18], we observed that the value of B-coefficient in aqueous urea solution at 1–5 m concentration range does not differ significantly from the value obtained at lower concentrations 0–1.5 m [20,21]. The reported B-coefficient value at infinite dilution for aqueous urea solutions is 0.038 and 0.035, respectively at 25°C [20,21]. The B-coefficient value obtained in this study at 35°C is ~ 0.053 (see Table II). This value is very similar to the value reported earlier. The positive B-coefficient value of aqueous urea solutions at 30–50°C were also obtained previously in this laboratory by Biswas [22]. From this positive B-coefficient data of urea in aqueous solution, one can conclude that urea tends to make water structure at the temperature range of 35–55°C.

The value of D-coefficient for urea in water were presented in Table II. The value is positive but irregular. The D-coefficient value indicates the solute–solute interactions coupled with size and shape effect of the solute and to some extent solute–solvent interactions. Due to lack of adequate theoretical knowledge, its significance is not fully understood [23]. The positive D value obtained in this case may represent that the increase in viscosity with the solute concentration is due to some additional factors other than the solute−solvent interactions (i.e., B-coefficient) which imparts negative contribution to the increase in viscosity.

Table III shows the free energy of activation ($\Delta G^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and activation entropies ($\Delta S^{\neq}$) for the viscous flow of urea solutions at different temperatures. It is seen that the $\Delta G^{\neq}$ of aqueous urea solutions increases with the concentration of urea at the studied temperature (Fig. 3). The activation free energy ($\Delta G^{\neq}$) shows little change until a concentration of about 1.5 m is reached. Beyond this concentrations, there is a large increase in $\Delta G^{\neq}$ with urea concentration. Although the increase does not seem to be very

TABLE II Viscosity coefficients B and D for urea in aqueous solutions at 35, 40 45, 50 and 55°C, respectively

35°C				40°C				45°C				50°C				55°C			
Con.[a] (mol dm^{-3})	*R.V.*,[b] η_r	*V.C.*[c]		*Con.*[a] (mol dm^{-3})	*R.V.*,[b] η_r	*V.C.*		*Con.*[a] (mol dm^{-3})	*R.V.*,[b] η_r	*V.C.*		*Con.*[a] (mol dm^{-3})	*R.V.*,[b] η_r	*V.C.*		*Con.*[a] (mol dm^{-3})	*R.V.*,[b] η_r	*V.C.*	
		B	D			B	D			B	D			B	D			B	D
0.9518	1.0536	0.0533	0.0018	0.9501	1.0536	0.0517	0.0022	0.9440	1.0530	0.0518	0.0045	0.9458	1.0631	0.0621	0.0005	0.9405	1.0619	0.0602	0.0007
1.8253	1.0996	0.0533	0.0018	1.8218	1.0928	0.0517	0.0022	1.8201	1.0954	0.0518	0.0045	1.8132	1.0963	0.0621	0.0005	1.8065	1.0942	0.0602	0.0007
2.6281	1.1490	0.0533	0.0018	2.6228	1.1537	0.0517	0.0022	2.6202	1.1637	0.0518	0.0045	2.6103	1.1804	0.0621	0.0005	2.6096	1.1732	0.0602	0.0007
3.3708	1.2116	0.0533	0.0018	3.3635	1.2035	0.0517	0.0022	3.3531	1.2135	0.0518	0.0045	3.3466	1.2184	0.0621	0.0005	3.3405	1.2098	0.0602	0.0007
4.0573	1.2420	0.0533	0.0018	4.0487	1.2446	0.0517	0.0022	4.0360	1.2467	0.0518	0.0045	4.0273	1.2526	0.0621	0.0005	4.0172	1.2560	0.0602	0.0007

[a]Con. Concentration; [b]R.V., Relative viscosity; [c]V.C., Viscosity Coefficient.

TABLE III Activation parameters [free energy ($\Delta G^{\neq}$), entropy ($\Delta S^{\neq}$) and enthalpy ($\Delta H^{\neq}$) of activation] for the viscous flow of urea in aqueous solutions

Concentration (mol kg^{-1})	$\Delta G^{\neq}$ *in* kJ mol^{-1} *at*					$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1} K^{-1})
	35 (°C)	40 (°C)	45 (°C)	50 (°C)	55 (°C)		
0.0000	9.0288	8.9034	9.8298	8.7395	8.6559	14.5577	18.2996
1.0000	9.0702	8.9707	9.8716	8.7788	8.7040	14.5125	17.7194
2.0008	9.1793	9.0653	9.0452	8.8992	8.8528	14.2245	16.4717
3.0000	9.2926	9.2070	9.1676	9.1022	9.0217	13.7827	14.5995
4.0007	9.4234	9.3168	9.2140	9.1830	9.0907	13.8025	14.5895
5.0000	9.4886	9.4042	9.3394	9.2570	9.1961	13.9629	14.5752

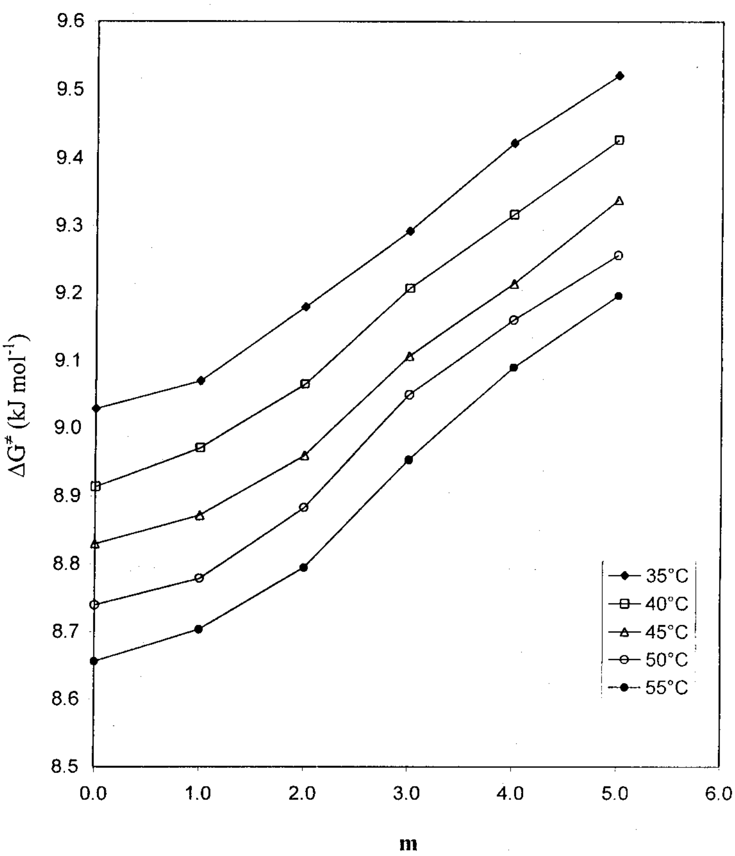

FIGURE 3 Plots of free energy ($\Delta G^{\neq}$) *versus* molality (m) for urea in aqueous solutions at 35, 40, 45, 50 and 55°C, respectively.

linear in the figure, it clearly indicates that the flow rate is not favoured energetically beyond 1.5 m urea concentration. The change may be attributed to the fact that $\Delta G^{\neq}$ is essentially constant or increase very little until urea clustering begins at about 1.5 m urea concentration i.e., above 1.5 m urea concentration cluster formation occurs. Since $\Delta G^{\neq}$ controls the rate of flow, which is governed by the slowest step in the fluid process, the data suggests that below 1.5 m urea there is essentially no effect on the fluid process of water. The slowest step in the fluid motion is dependent on the case with which translation of the principal kinetic entity occurs. The data suggests that this entity may likely to be water itself below 1.5 and above 1.5 m urea, the principal kinetic entity for fluid flow in an aggregate of urea and water.

The concept of cluster formation above 2 m urea concentration was proposed by Vold *et al.* [24] from the NMR studies of rates of protolysis of urea. He suggested that the formation of urea aggregates occur above 2 m urea concentration. The increase of $\Delta G^{\neq}$ with molality of urea is an indication of structure making properties of urea in aqueous solutions. Similar structure making behaviour of some electrolytes have been reported by other authors elsewhere [25,26].

Variation of the entropy of activation ($\Delta S^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) with concentration of urea is shown in Figs. 4 and 5. The $\Delta S^{\neq}$ and $\Delta \mathrm{H}^{\neq}$ for the viscous flow decreases with the increase of concentration of urea. This decrease of $\Delta S^{\neq}$ indicates the structural ordering (making) effect of urea in aqueous solutions. Thus the volumetric, viscometric and thermodynamic data of aqueous urea solutions strongly supports the view that urea acts as a net structure maker at the temperature range of 35–55°C. The "structure forming" tendency of urea in aqueous solution is further supported by the apparent molal heat capacity data as follows.

The structure making solute when dissolved in water increases the ice like [27] nature of water and the melting of such structure requires greater energy with the result that such solutes give rise to positive excess partial molal heat capacities (ΔC_{ρ}^{o}) [17]. The reverse is true for structure breaking solutes. From the studies on heats of solution and proton chemical shift, Subramanian *et al.* [14] reported the limiting excess heat capacities ΔC_{ρ}^{o} of urea as $3.9 \pm 7\,\mathrm{cal\,mol^{-1}\,deg^{-1}}$ at 30°C, $0.0 \pm 6\,\mathrm{cal\,mol^{-1}\,deg^{-1}}$ at 20°C and $-6.0 \pm 5\,\mathrm{cal\,mol^{-1}\,deg^{-1}}$ at 12°C, respectively. Gucker *et al.* [16] reported the ΔC_{ρ}^{o} of urea

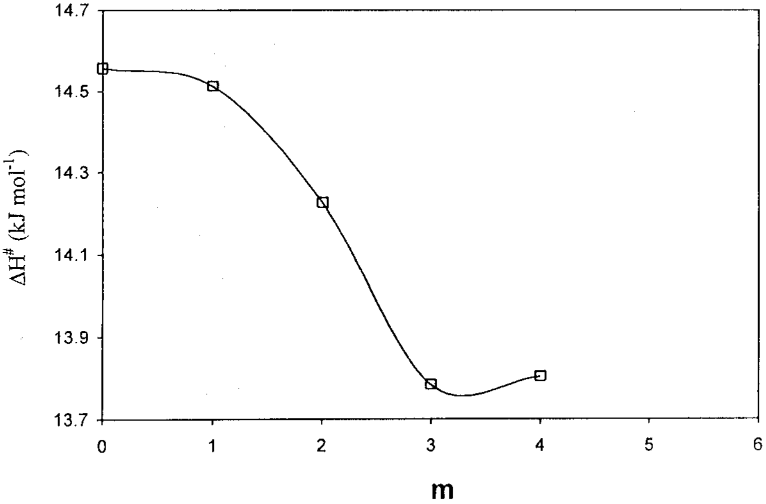

FIGURE 4 Plot of enthalpy of activation ($\Delta H^{\neq}$) *versus* molality (m) for urea solutions.

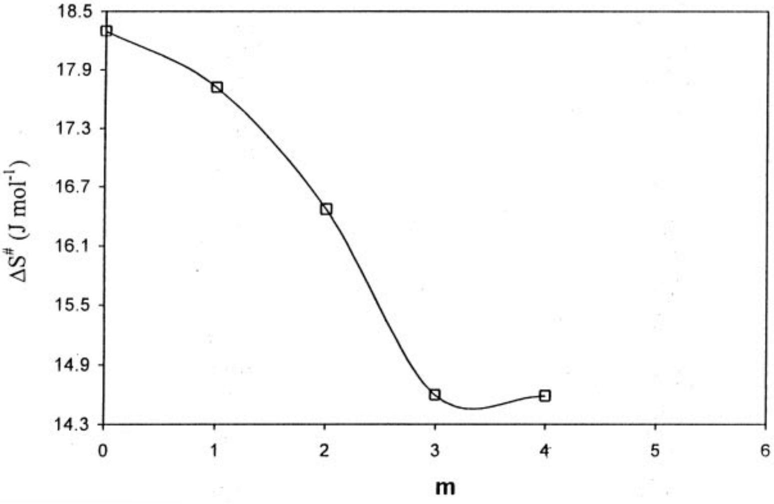

FIGURE 5 Plot of entropy of activation ($\Delta S^{\neq}$) *versus* molality (m) for urea solutions.

as 22.85 ± 7.8 cal $\mathrm{mol^{-1}\,deg^{-1}}$ at 40°C, 20.85 ± 7.3 cal $\mathrm{mol^{-1}\,deg^{-1}}$ at 30°C, 18.50 ± 7.4 cal $\mathrm{mol^{-1}\,deg^{-1}}$ at 20°C, 13.86 ± 7.7 cal $\mathrm{mol^{-1}\,deg^{-1}}$ at 10°C, 10.71 ± 13.2 cal $\mathrm{mol^{-1}\,deg^{-1}}$ at 5°C and 8.64 ± 7.3 cal $\mathrm{mol^{-1}\,deg^{-1}}$ at 2°C, respectively. The value of ΔC_{ρ}^{o} reported by these two research groups differ significantly at the same temperature. Subramanian *et al.* [14] determined the ΔC_ρ^o value directly from integral heats of solution measurements at very low concentration which neither involves any uncertainty in extrapolation nor requires the knowledge of accurate values of the C_ρ of urea. But Gucker *et al.* [16] estimated the value of ΔC_ρ^o from the extrapolation of ϕ_{c_ρ} as a function of square root of molality to infinite dilution from large concentration and therefore ΔC_ρ^o of urea in aqueous solution at lower temperature might be subject to uncertainty. The ΔC_ρ^o values at 30°C obtained from both the studies are positive indicating that urea has a net structure making properties [17]. This observation is consistent with the result obtained here in this study. The decrease of ΔC_ρ^o value with the decrease in temperature (0.0 at 20°C and negative at 12°C) [14], indicates that urea tends to make water structure at and above 20°C and tends to break the water structure below 20°C temperature.

CONCLUSION

From this study, we can conclude that structure making or breaking property of urea in aqueous solution is a temperature dependent property. Urea behaves as a structure maker at and above the temperature of 35°C. Probably this structure making property of urea may take out water from interaction zone of protein/enzyme, thereby inducing denaturation of the protein/enzymes in aqueous–urea solution at the physiological pH and temperature.

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