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Effect of Urea, its Concentration and Temperature on Water Structure

MAN SINGH* and BABU RAM

Centre for Surfactants and Plasticizers Research
Department of Chemistry
Deshbandhu College (University of Delhi), New Delhi-110 019, India

The investigations on the peculiar behaviour of urea and its concentration in aqueous solutions have been studied in terms of precisd density and viscosity measurements at 288.15, 298.15 and 308.15 K, up to 7 m (mol kg^{-1} of urea) aqueous urea solutions. These data were processed to evaluate the limiting apparent molar volumes (ϕ_V) and viscosity B- and D-coefficients. The results of the experimental measurements were discussed in terms of ϕ_V^0, B- and D-coefficients. The effect of urea and its concentration on water structure was attributed to the dimer and trimer formation of urea molecules. The stability of dimer and trimer formation of urea molecules in water seems to be significantly affected by temperature.

INTRODUCTION

A study of thermodynamic properties of model compounds in aqueous urea solutions is fundamental to an understanding of urea denaturation of the proteins. It is generally accepted that urea does not appreciably interact with either hydrophobic or hydrophilic[1] molecules or groups and acts mainly to disrupt[2] H-bonding among water molecules in aqueous medium. It is observed that urea and water combine to form more clusters[3] than water alone with the formation of interstices.[2]

EXPERIMENTAL

Urea (m.p. 132.7°C) was obtained from BDH AnalaR grade and was dried at 373.15 K in vacuum desiccator over phosphorus pentoxide for 24 h and stored in a dry box until used. Demineralised double distilled water was used for solution preparation by weight. The densities were measured with an Antom Paar vibrating tube digital densimeter (DMA 601/60) and viscosities with a common Ubbelohde viscometer. The temperature for density and viscosity measurements was controlled precisely to ± 0.01°C. Higher temperature range was obtained by a comparative calibration of Beckmann thermometer with temperature controlling unit of densimeter. Specifical glasswares were fabricated according to need.

RESULTS AND DISCUSSION

The density (ρ) data (Table-1) for various aqueous urea solutions at 288.15, 298.15 and 308.15 K have been processed to calculate apparent molal volumes (ϕ_v) as

$$\phi_v = \frac{1000(\rho - \rho_0)}{m_2 \rho \rho_0} + \frac{M_2}{\rho} \tag{1}$$

where ρ_0 and ρ are solvent and solution densities respectively and m_2, M_2 are solution molality and solute molar mass respectively. The concentration of urea m_2 is expressed as mol kg^{-1} (of solvent). The ϕ_v values of urea in water are plotted in Fig. 1 against its molality, where the lines represent the least square best fit.

$$\phi_v = \phi_v^0 + Am \tag{2}$$

where A is the experimental slope, ϕ_v^0 the limiting apparent molal volumes of urea in aqueous solution, evaluated from the extrapolation of ϕ_v by the least square method as given in Table-1.

Water-urea system is of great interest since the dielectric constant (D) of the mixture[4] do not change much from that of water over certain concentration range, *e.g.*, D of 3 m urea solution is only about 8% higher[4] than that of H_2O. It seems that solute-solvent interaction transfer coefficients decrease with decrease in the structural hydration of the solute. Effect of urea on the structure of water and hydrophobic bonding has been considered by several workers[2, 5, 6]. Krescheck and Scherag[7], following Schellman[8] assumed that in water, urea forms dimer, trimer, etc.

$$U + U \rightleftharpoons UU \text{ (dimer)}$$
$$UU + U \rightleftharpoons UUU \text{ (trimer)}$$

Also, since (bulk) water is essentially tetrahedral in geometry, and urea triangular in framework, this bars molecules of the latter from entering the bulk water phase, but dissolves in the dense phase. Making a simplified assumption that only constituents need to be considered and that mole fraction of bulky (f) and dense water (1 – f) is related by equilibrium constant (K),

$$\underset{(H_2O)_{bulky}}{f} \rightleftharpoons \underset{(H_2O)_{dense}}{(1-f)} \tag{3}$$

$$K = \frac{f}{1-f} \tag{4}$$

This effect is rather subtle and is in contrast to direct structure breaking action such as those ascribed to ions[9] which creates torque and produces region of misfit. The structure breaking effect of urea on the other hand is considered to be a statistical-thermodynamic concept[2, 10] and is structure breaking in result rather than in mechanism. Urea molecules in water show a weak structure-breaking effect arising due to its dissolution in dense-water and shifting the

$$(H_2O)_{bulky} \rightleftharpoons (H_2O)_{dense}$$

equilibrium to the right, which is referred to as of statistical thermodynamic origin.

TABLE-1
DENSITIES (ρ), APPARENT MOLAL VOLUMES (ϕ_v) OF AQUEOUS UREA SOLUTIONS AT 288.15, 298.15 AND 308.15 K

m (mol kg^{-1})	c (mol l^{-1})	ρ (g cm^{-3})	ϕ_v (cm^3 mol^{-1})	$\Delta\phi_v$ (cm^3 mol^{-1})
T = 288.15 K				
0.8581	0.8259	1.01208	44.31	0.02
1.6332	1.5215	1.02296	44.38	0.01
2.9602	2.6134	1.03982	44.49	-0.02
2.6967	2.4061	1.03673	44.44	-0.05
3.2589	2.8433	1.04323	44.56	0.17
3.9019	3.3206	1.05043	44.62	0.02
5.1091	4.1553	1.06289	44.74	0.00
6.6990	5.1460	1.07724	44.91	0.00
T = 298.15 K				
0.1493	0.1479	0.99941	44.21	-0.07
0.2375	0.2343	1.00076	44.36	0.08
0.3246	0.3191	1.00214	44.24	-0.05
0.6865	0.6644	1.00762	44.28	-0.04
0.7950	0.7657	1.00922	44.29	-0.04
1.2717	1.2893	1.01736	44.43	0.05
2.3783	2.1448	1.03065	44.52	0.05
2.7533	2.4460	1.03530	44.55	0.04
6.2142	4.8478	1.01270	44.88	0.05
8.4480	6.1092	1.09006	44.97	-0.07
T = 308.15 K				
0.4136	0.4037	1.00034	44.71	-0.17
0.8581	0.8215	1.00666	44.95	0.04
1.4274	1.3336	1.01437	45.08	0.11
1.6332	1.5130	1.01726	44.98	-0.01
2.9602	2.5968	1.03320	45.25	0.15
1.6632	2.3919	1.03064	45.03	-0.05
2.6967	2.8261	1.03694	45.45	0.02
6.6990	5.1148	1.07070	45.34	-0.08

$\Delta\phi_v = \phi_v$ (obs) $- \phi_v$ (calc)

ϕ_v (calc) at a given m was obtained from regression analysis of data into $\phi_v = \phi_v^0 + S_vC$.

Temperature (K)	ϕ_v^0 (cm^3 mol^{-1})	$\sigma\phi_v^0$ (cm^3 mol^{-1})	A′	σA′
288.15	44.15	0.02	0.14	0.01
298.15	44.23	0.02	0.12	0.01
	44.23*	0.01	0.12	0.01
303.15	44.63*	0.01	0.08	0.01
308.15	44.86	0.11	0.10	0.01

*Calculated from data of F.T. Gucker, F.W. Gage and Moser. (Ref No. 4)

Millero *et al.*[11] considered PMV of a non-electrolyte to be made up of an intrinsic volume of the solute ($\overline{V}^0_{int}$) and the volume change (shrinkage) due to its interaction with the solvent.

Shahidi *et al.*[12] calculated the $\overline{V}^0_{int}$ as

$$\overline{V}^0_{int} = \overline{V}^0_{vw} + \overline{V}^0_v \qquad (5)$$

where $\overline{V}^0_{vw}$ and $\overline{V}^0_v$ are Vander Waals volume and Voids volume respectively.

A shrinkage volume (V_s) of the solute was of the origin of hydrogen bonding

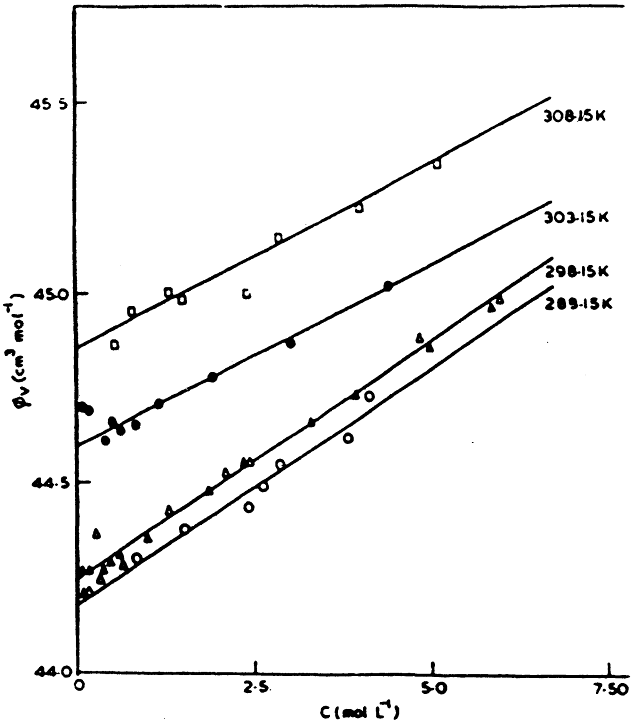

Fig. 1. Plot of ϕ_v *vs*. C of urea solution at 288.15 K (O); 298.15 K (Δ); 308.15 K (□); 298.15 K (▲) (F.T. Gucker); 303.15 K (•) F.T. Gucker

groups in the solute with water molecules. Urea molecules break down the hydrogen bonded structure of water.

$$\phi_v^0 = \overline{V}_2^0 = \overline{V}_{vw}^0 + \overline{V}_v^0 - V_s \qquad (6)$$

Urea-urea and urea-water interactions would weaken at higher temperatures.

Urea in water is weak solvating and weak hydrophobic interactions through hydrogen bonding of urea (Fig. 1).

More elaborately changes in PMV ($\overline{V}_2^0 = \phi_v^0$) of urea with its increasing concentration in aqueous solution have been considered as

$$\overline{V}_2^0 = \overline{V}_{vw}^0 + \overline{V}_v^0 + \overline{V}_{elect}^0 \qquad (7)$$

where $\overline{V}_{elect}^0$ is the volume of electrostriction of urea in water.

The viscosity data (Fig. 2) for water of urea solutions at 288.15, 298.15 and 308.15 K were obtained to examine how far the data in this study agreed with the available literature values. Trend of variations η–c data is shown in Fig. 2. Data of Kawahara and Tanford at 298.15 K are included for comparison. These data could be least square fitted into the Jones-Dole equation:

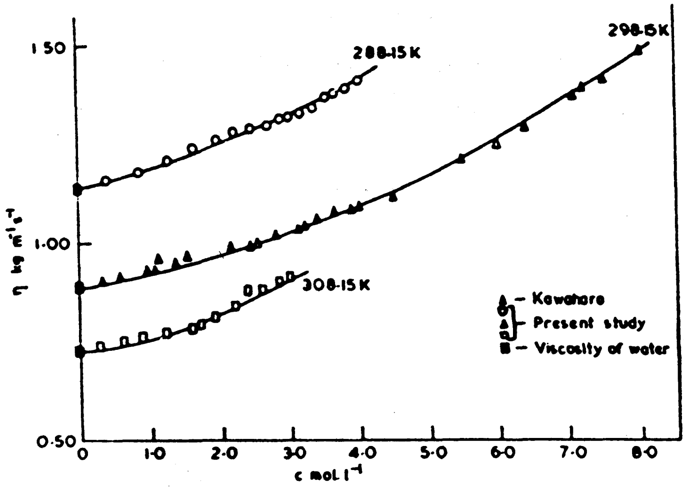

Fig. 2 Plot of η (viscosity) vs C of urea in aqueous solution.

$$\eta_r = 1 + Bm + Dm^2 \qquad (8)$$

where B and D are viscosity coefficients.

In view of the low magnitude of D and the considerable observed scatter in its values, and also considering that its significance is not completely understood[13], only the variations in B-coefficients have been considered in discussing the results. At a given temperature, η is seen to increase with increase in urea concentration (Fig. 2) and at a given urea concentration, η decreases with increasing temperature. It was observed that η of urea-water solutions are slightly higher than that of water at all the temperatures. Low η and also B- and D-coefficients (Table-3) for urea-water solutions are attributed to the hydrodynamic theories. Urea flow creates low torsional forces. Urea breaks water structure and this effect goes on with urea concentration. At higher temperatures dimer and trimer formations also decreases and hence η decreases with temperature (Fig. 2).

Conclusion

ϕ_v Values (Table-1) with its concentration at fixed temperature increase slightly (Fig. 1). ϕ_v values also slightly increase with temperature. But increase in ϕ_v from 288.15 K to 298.15 K is of very low degree. While there is appreciable increase in ϕ_v from 298.15 K to 308.15 K, low degree of variation in ϕ_v values of urea in aqueous solution with its concentration at lower temperature region, *i.e.*, from 288.15 K to 298.15 K, highlights the mild structure breaking effect on water and making a network structure with water molecules. At 308.15 K water molecules themselves get mechanically broken and urea and its concentration enhances this effect at higher temperature. It seems that urea network structure with water also gets affected and molecular volume slightly expands (Fig. 1) in water with its concentration. The variation in the value of $\overline{V}_s^0$ with urea concentration at fixed and varied temperature decreases. The trend of ϕ_v variation with urea concentration in aqueous solutions at fixed temperature and varied temperature seems to favour less interactions of urea molecules with water.

These ϕ_v values are supported by the η values of urea in aqueous solutions. η values at any temperature increase with urea concentration in aqueous solutions (Table-2). η values decrease with temperature (Table-2). Decreasing trend (Fig. 2) of η of urea with temperature is attributed to the deformation of dimer and trimer and weakening of hydrogen network of urea molecules with water molecules; hence almost independent urea molecules in aqueous solution can cause less transitional forces and require less activation energy, so easily flow by reducing η with temperature of aqueous urea solutions. But higher urea concentration may develop the possibility of hydrogen network and comparatively dimer and trimer stability. B- and D-values (Table 3) values for urea in aqueous solutions are of low degree. With temperature B-values decrease, which seems to be expected. Both B- and D-values of urea in aqueous urea solutions. Support the above said structure dynamics of water-urea solutions.

TABLE-2

VISCOSITY DATA OF AQUEOUS UREA SOLUTIONS AT 288.15, 298.15 AND 308.15 K

m_{urea} (mol kg^{-1})	c (mol L^{-1})	ρ (g cm^{-3})	η (kg m^{-1} r^{-1})	η_r	$\Delta\eta_r$
T = 288.15 K (η_0 = 1.139 kg m^{-1} s^{-1})					
0.4191	0.4111	1.00575	1.1632	1.0212	0.0012
0.8802	0.8464	1.01243	1.1873	1.0424	0.0012
1.2625	1.1944	1.01779	1.2130	1.0658	0.0014
1.6177	1.5026	1.02256	1.2418	1.0903	0.0061
1.9519	1.9744	1.02707	1.2602	1.1064	0.0024
2.2292	2.0263	1.03066	1.2816	1.1252	0.0045

2.4624	2.2173	1.03362	1.2939	1.1360	0.0011
2.6900	2.4003	1.03644	1.3044	1.1453	0.0037
2.8506	2.5274	1.03840	1.3233	1.1609	0.0018
3.0376	2.6734	1.04065	1.3245	1.1629	–0.0079
3.1859	2.7876	1.04241	1.3337	1.1710	–0.0093
3.3575	2.9182	1.04441	1.3466	1.1823	–0.0090
3.5342	3.0507	1.04644	1.3705	1.2033	0.0005
3.6941	3.1692	1.04825	1.3862	1.2170	0.0038
3.8269	3.2665	1.04973	1.3975	1.2269	0.0050
3.9746	3.3735	1.05136	1.4100	1.2379	0.0063
T = 298.15 K (η_0 = 0.8903 kg m^{-1} s^{-1})					
0.3437	0.3500	1.00264	0.9049	1.0164	–0.0002
0.6014	0.6197	1.00655	0.9160	1.0289	–0.0007
0.9377	0.9815	1.01170	0.9309	1.0457	–0.0002
1.3711	1.4648	1.01838	0.9505	1.0677	0.0002
1.7788	1.9380	1.02469	0.9710	1.1121	–0.0223
2.1638	2.3874	1.03050	0.9901	1.1123	–0.0011
2.5232	2.8519	1.03629	1.0012	1.1246	–0.0029
2.8522	3.2780	1.04142	1.0247	1.1509	0.0002
3.1650	3.6966	1.04629	1.0386	1.6660	0.0033
3.4218	4.0506	1.05028	1.0603	1.1910	–0.0053
3.6644	4.3940	1.05403	1.0791	1.2121	–0.0112
3.9002	4.7365	1.05767	1.0770	1.2097	0.0063
T = 308.15 K (η_0 = 0.7194 kg m^{-1} s^{-1})					
0.0804	0.0797	0.99530	0.7224	1.0042	0.0002
0.3013	0.2956	0.99895	0.7452	1.0358	0.0203
0.6474	0.6255	1.00378	0.7533	1.0471	0.0113
0.9460	0.9186	1.00811	0.7655	1.0641	0.0075
1.2827	1.2056	1.01237	0.7712	1.0720	–0.0071
1.5386	1.4306	1.01572	0.7860	1.0926	–0.0060
1.8468	1.6951	1.01969	0.7956	1.1059	–0.0174
2.1211	1.9250	1.02313	0.8112	1.1276	–0.0189
2.4356	2.1821	1.02700	0.8491	1.1804	0.0060
2.7235	2.4119	1.03047	0.8817	1.2256	0.0248
3.0220	2.6446	1.03398	0.8940	1.2427	0.0135
3.2767	2.8389	1.03691	0.9025	1.2546	0.0005
3.4985	3.0050	1.03941	0.9123	1.2682	–0.0078

$\eta_r = \eta/\eta_{solvent}$ $\Delta\eta_r = \eta_r\,(obs) - \eta_r\,(calc)$

η_r (calc) was obtained from regression analysis of $\eta_r - c$ data in Jones-Dole eqn in the form: $\eta_r = 1 + Bc + Dc^2$.

TABLE-3
UREA-WATER SYSTEM

Least-square fit of η_r-c data into Jones-Dole equation
$\eta_r = 1 + Bc + Dc^2$

Temperature (K)	B	σB	D	σD
288.15	0.0458	0.0067	0.0028	0.0010
298.15	0.0464 0.0380[a]	0.0051	0.0032 0.0021[a]	0.0014
308.15	0.0481	0.0145	0.0084	0.0032

[a] Kawahera and Tanford, *J. Biol. Chem.*, **241**, 3228 (1966).

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