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Internal pressure, free volume of aqueous urea solutions at different temperatures

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ABSTRACT

Nitrogen is needed by all plants and usually in large quantities. In fact, nitrogen is so important to plant growth and thus to food and fiber productions. Urea is the world's most common nitrogen fertilizer and has been used uniformly in all the agricultural lands of the world. Urea is soluble compound and easily gets along with water. The chemical structure of urea helps it to be soluble enough as the hydrogen bonds with water molecules, each forming two bonds with oxygen. In the present work, ultrasonic velocity, density and viscosity of aqueous solutions of urea were measured at various temperatures from 303˚K to 323˚K. The internal pressure (π_i)*, osmotic pressure* (π)*, free volume* (V_f)*,* $\Delta\pi_i$*, molar cohesive energy (MCE), gibb's free energy* (ΔG) *of the solutions were computed. From the variations of the values with the concentration and temperatures of the solutions the interaction between water and urea is studied. The concentration dependence of viscosity was explained by Jones-Dole equation. The coefficients A and B the above equation have been studied at different temperatures.* $\Delta\pi_i$ *has been evaluated in each system which gives an idea about the effect of cohesive forces in ion-solvent interaction. It is understood that sensitive information regarding the cohesive forces is well obtained by the data* $\Delta\pi i$ *instead of the coefficients A and B of the Jones-Dole equation.*

Key words: Internal pressure, free volume, molar cohesive energy, Jones Dole equation.

INTRODUCTION

The study of the properties of aqueous solutions is very important in many areas of science and researches. Science and technology of ultrasonic is widely sought in the recent years for industrial and medical applications. The study of intermolecular interaction plays an important role in the development of molecular sciences. The coefficients A and B of the Jones-dole equation for the given solute-solvent systems under study have been evaluated. The valuable information on inter-ionic contribution of electrolytic forces, order and disorder introduced by the ions into the solvent structure, the qualitative assessment of violent thermal agitation at higher temperatures, the way in which anion-anion interact and cation-cation interact, all these conclusions are obtained by the manner in which A and B values vary with temperature in this system[1]. The investigation of thermodynamic properties of aqueous urea solutions has been the area of interest of a number of researchers.[2-4]

EXPERIMENTAL SECTION

The ultrasonic velocity was measured using a single crystal variable path interferometer working at 2 MHz by standard procedure. The accuracy of ultrasonic velocity determination in the solution is ±0.5%. The velocities were measured at various temperatures from 303˚K to 323˚K. The densities were measured using a specific gravity bottle by relative measurement method and the viscosity was measured using Ostwald's viscometer with an accuracy of $\pm$ 0.1%. The temperature is maintained using temperature bath with an accuracy of $\pm$0.1°C.

COMPUTATIONAL METHODS:

The thermodynamical parameters such as the internal pressure (π_i), osmotic pressure (π), free volume (V_f), $\Delta\pi_i$, molar cohesive energy (MCE), gibb's free energy (ΔG) have been calculated using the experimental data of velocity of sound (U), density (ρ), and viscosity (η) by the follwing equations,

1. Internal pressure $\pi_i = bRT^* (K\eta/U)^{1/2} {}^*(\rho^{2/3}/M^{7/6})$ (N/m^2)
2. Free volume $V_f = (MU/K\eta)^{3/2}$ (m^3)
3. Osmotic pressure $\pi = nRT/V$ (mmHg)
4. $\Delta\pi_i = \pi_i - \pi_o$
5. Cohesive energy $MCE = \pi_i * V_m$ ($KJ\ mol^{-1}$)
6. Gibb's free energy $\Delta G = -KT \ln (KT\tau/h)$ ($KJ\ mol^{-1}$)

Where, b = 2 cubic packing factor, T- absolute temperature,
K= $4.28*10^9$ dimensionless temperature independent constant,
R = Molar gas constant, η – viscosity, U – ultrasonic velocity,
M – effective molecular weight of the solute, ρ – density,
n - number of solute particles, V – volume of the solution,
π_o – internal pressure of the solvent,
h - Plank's constant, τ – relaxation time.

RESULTS AND DISCUSSION

The measurement of internal pressure is important in the study of the thermodynamic properties of solutions. The internal pressure is the cohesive force, which is the resultant force of attraction and force of repulsion between the molecules. Internal pressure also gives an idea of the solubility charcteristics. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent arise through hydrogen bonding, charge tranfer, columbic or Van der Waal's interaction. The internal pressure is the single factor which varies due to all type of solvent-solvent, solute-solute, and solvent-solute interactions. The internal pressure of hydrogen bonded liquids is large as compared to non–hydrogen bonded liquid. Hence internal pressure in solution can be used for studying the molecular association through hydrogen bonding[5]. In this present study the internal pressure decreases with increase in concentration indicates the decrease in cohesive forces leading to breaking the structure of the solute. Due to weakening of intermolecular forces of attraction the internal pressure should fall. Decrease in internal pressure indicates that there is a weak interaction between solute and solvent molecule[6].

The molecules of liquid are not closely packed and as such there is always some free space between them. This free space is known as free volume. The free volume is one of the significant factors in explaining the variations in the physico-chemical properties of solutions. The free space and its dependent properties have close connection with molecular structure and it may show interesting features about interactions of solutions[7]. The free volume increases with increase in concentration. The decrease in molecular association causes an increase in free volume. The increase in freevolume may be attributed to lose packing of the molecules inside the shield, which may be brought about by weaking of molecular interactions. Thus free volume is an inverse function of internal pressure. Hence increase in free volume causes internal pressure to decrease, which indicates the existence of solute-solvent interactions.

Free volume and internal pressure are fundamental properties of the liquid state that has been studied initially by Hildebrand etal.[8-9] and subsequently by several workers. As observed in this work, the internal pressure decreases at lower concentration and increases at higher concentrations. The free volume found to decrease at higher concentration and increases at lower concentration. Ion solvent interaction is affected by two factors.
(i) The breaking up of the solvent structure on addtion of solute to it and
(ii) The solvation of solute.

The decrease of V_f (increase of π_i) indicates the formation of hard or tight solvation layer around the ion and increase of V_f (decrease of π_i) may be due to formation of thin or loose solvation layer[10]. The variation of internal pressure and free volume with concentration is shown in fig(1) and fig(2) respectively and the values are tabulated in table.1.

Suryanarayanan C.V. and Kuppuswamy (1981) have found that at a given temperature a general equation of the form $\pi_i = \pi_o + Am^2 + Bm$ where π_o is the internal pressure of the solvent, m is the molality A and B are depedent on temperature.[11]. Thus the effect of repulsive forces or cohesive forces in ion-solvent interaction is very well understood by $\Delta\pi_i$.

The difference in the internal pressure $\Delta\pi_i = \pi_i - \pi_o$ of the solution and the solvent can be positive or negative depending upon the electrolyte. Figure 3 shows the variation of $\Delta\pi_i$ with concentration. For urea, $\Delta\pi_i$ is found to be negative almost for all concentrations indicating that the internal pressure of the solvent, (water) is lowered due to its addition.This may be due to the cohesive forces may get loosened perhaps by breaking hydrogen bonds in water. In the present work, it is found by observation that the change in internal pressure $\Delta\pi_i$ of the system urea shows the pre-dominance of repulsive force as $\Delta\pi_i$ is more negative and the results are presented in the table 1.

The coefficients A and B in the equation determine the sign of $\Delta\pi_i$. In aqueous urea solutions A is found to be positive at all temperatures and becomes negative at 318˚K. But only the coefficient B determines the sign of $\Delta\pi_i$. The values of constant A and B computed at different temperatures are given in table 2.

A similar relation holds for the free volume $V_f = V_f(o) + Cm^2 + Dm$. Here $V_f(o)$ is the free volume of the solvent. The arbitrary coefficients C and D are dependent on temperature. The values C and D are calculated at all temperatures and are given in table 2.

The viscosity A and B coefficients for the urea aqueous solutions are calculated from the Jones-Dole equation $\eta/\eta_0 = 1 + Am^{1/2} + Bm$ where η and η_0 are the viscosities of the solution and solvent respectively and m is the molal concentration of the solute. A is determined by the ionic attraction theory of Falkenhagenveron also called Falkenhagen coefficient. B is Jones-Doles coefficient is an empirical constant determined by solute-solvent interactions. It is observed that the values of viscosity are increases with increase in concentration of aqueous urea solutions. This increasing trend indicates the existence of molecular interaction occuring in this systems. It is observed that the values of A are negative at all temperatures and becomes positive at higher temperatures and B coefficient are positive and becomes negative at 323˚K. Since A is a measure of ionic interaction, it is evident that there is a weak ion-ion interaction in the mixtures studied, which is indicated by the smaller magnitude of A values. B coefficient is also known as measure of order and disorder introduced by the solute into solvent. It is also a measure of solute-solvent interaction and relative size of the solute and solvent molecules. The behaviour of B coefficient at all temperatures suggests the existence of strong solute-solvent interaction.[12]

The osmotic pressure is defined to be the pressure required to maintain an equilibrium with no net movement of solvent. Osmotic pressure is a colligative property meaning that the property depends on the molar concentration of solute but not on its identity. The substance in aqueous solution lower the free- energy status of solvent molecules and the resulting osmotic pressure of the solution can be derived from physical chemistry.

Osmotic pressure generated by a salt that dissociates into ions in aqueous solution, or by undissociated organic molecules in solution can be calculated from the historic Van Hoff expression ($\pi = nRt/V$). This relates osmotic pressure of an ideal solution to the concentration of that solute expressed in terms of osmolality and RT. The osmotic pressure value increases with the increase of concentration and also increases with the increase of temperature. The variation of osmotic pressure with concentration is shown in fig 4. Osmotic pressure is almost independent of temperature at all concentrations were studied.

The concept of molar cohesive energy has been used by several researchers for comparing the interactions in the liquid mixtures[13-16]. It is usually given as a product of internal pressure (π_i) and molar volume (V_m). MCE= $\pi_i * V_m$. A molecule containing strong polar groups exerts corresponding strong attractive forces on its neighbours. If the intermolecular forces are small, the cohesive energy is small, the cohesive energy is low and the molecules have relatively flexible chains. The cohesive energy values show a similar value as that of internal pressure. The fig 5 exhibits the variation of cohesive energy with concentration.

The relaxation time for a given transition is related to the activation free energy. The variation of relaxation time with temperature can be expressed in the form of Eyring salt process theory $1/\tau = KT/h \exp(-\Delta G/KT)$.

The above equation can be rearranged as $\Delta G = -KT \log(h/KT\tau)$ where K is the Boltzmann constant and h is the plank's constant. The Gibb's free energy shows a similar behaviour as that of a cohesive energy. At lower concentrations, the gibb's free energy is decreases with increase of concentration and increases at higher concentrations. The decrease of gibb's free energy favours the formation of products after reaction.[17] Gibb's free energy decrease with an increase of temperature. This variation of gibb's free energy is shown in fig 6.

Table 1. Values of internal pressure, free volume, osmotic pressure, $\Delta\pi_i$, molar cohesive energy and gibb's free energy of urea solutions at different temperatures

Con (m)	Π_i (10^8) N/m^2	V_f (10^{-8}) m^3	π (mmHg)	$\Delta\pi_i$	MCE (10^4 KJ mol^{-1})	ΔG (10^{-21} KJ mol^{-1})
303˚K						
0.3	25.8882	2.2141	7.4350	-0.0913	4.7235	4.6099
0.6	25.4319	2.2708	14.5876	-0.5477	4.7059	4.5763
0.9	25.2054	2.3184	21.1891	-0.7742	4.6782	4.4846
1.2	25.1982	2.2953	27.8482	-0.7813	4.7024	4.5271
1.5	25.8550	2.0818	34.6413	-0.1245	4.8745	4.8286
1.8	26.0455	2.0203	40.8827	0.0658	4.9300	4.8885
2.1	26.0152	1.9951	46.6138	0.0355	4.9639	4.9543
308˚K						
0.3	24.6613	2.6835	7.55777	-0.2939	4.5053	4.1823
0.6	24.2852	2.7205	14.8283	-0.6700	4.5090	4.1873
0.9	24.0845	2.7694	21.5388	-0.8707	4.4877	4.1106
1.2	24.2849	2.6701	28.3078	-0.6703	4.5515	4.2361
1.5	24.3193	2.6145	35.2130	-0.6359	4.5963	4.3205
1.8	24.5140	2.5211	41.5574	-0.4412	4.6621	4.4201
2.1	25.1397	2.3027	47.3831	0.1844	4.8171	4.6980
313˚K						
0.3	23.7980	3.1062	7.68047	-0.2608	4.3670	3.9148
0.6	23.4564	3.1655	15.0690	-0.6024	4.3573	3.8597
0.9	23.3830	3.1723	21.8884	-0.6758	4.3595	3.8553
1.2	23.6755	3.0197	28.7674	-0.3833	4.4406	4.0148
1.5	23.7012	2.9457	35.7846	-0.3576	4.4936	4.1273
1.8	24.3438	2.6987	42.2320	0.2850	4.6323	4.3677
2.1	24.6837	2.5443	48.1523	0.6249	4.7379	4.5639
318˚K						
0.3	23.1525	3.525	7.8031	-0.1013	4.2562	3.6645
0.6	22.7833	3.5988	15.3097	-0.4705	4.2463	3.6186
0.9	23.2576	3.3691	22.2380	0.0037	4.3437	3.8094
1.2	23.2290	3.3297	29.2268	-0.0248	4.3720	3.8749
1.5	23.2717	3.2687	36.3562	0.0179	4.4085	3.9378
1.8	23.6472	3.0687	42.9066	0.3933	4.5137	4.1306
2.1	23.9567	2.8943	48.9214	0.7028	4.6176	4.3363
323˚K						
0.3	22.6557	3.9275	7.9258	0.0874	4.1727	3.4728
0.6	22.1683	4.0736	15.5504	-0.3999	4.1419	3.3762
0.9	22.1839	4.0621	22.5877	-0.3843	4.1463	3.3833
1.2	22.1228	4.0144	29.6864	-0.4454	4.1767	3.4432
1.5	21.9805	4.0434	36.9278	-0.5877	4.1751	3.4374
1.8	21.8051	4.0879	43.5813	-0.7631	4.1690	3.4113
2.1	22.0447	3.8824	49.6906	-0.5235	4.2546	3.5925

Table 2. Values of internal pressure A & B coefficients, free volume C & D coefficients and viscosity A & B coefficients of Jones – Dole equation of aqueous urea solutions at different temperatures

	Internal pressure π_i		Free volume V_f		Jones-Dole equation	
Temperature (˚K)	Constant A	Constant B	Constant C	Constant D	Coefficient A ($A/dm^{3/2}.mol^{-1/2}$)	Coefficient B ($B/dm^3.mol^{-1}$)
303˚K	0.7167	-1.5191	-0.1532	0.2402	-0.0597	0.1019
308˚K	0.8095	-1.2503	-0.2638	0.2565	-0.0307	0.0802
313˚K	0.7741	-1.1283	-0.5248	0.5874	-0.0400	0.0977
318˚K	-0.1052	0.0860	0.0794	-0.2724	0.0425	0.0552
323˚K	0.2242	-0.6410	0.0851	-0.0648	0.0843	-0.0381

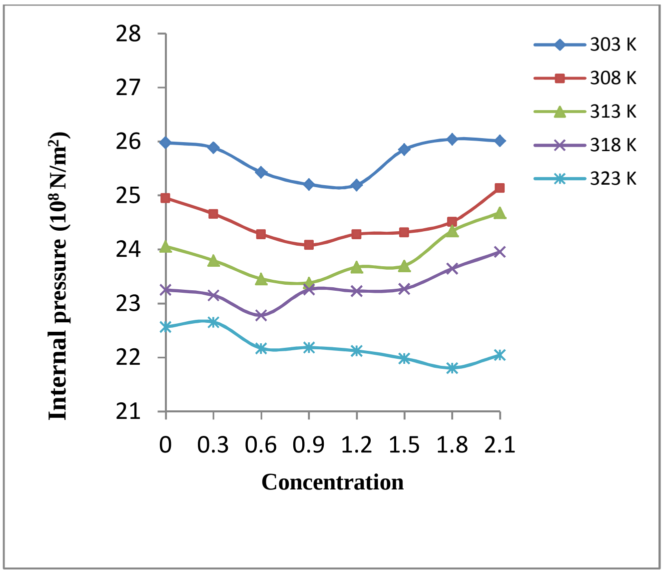

Fig 1. Concentration Vs Internal pressure

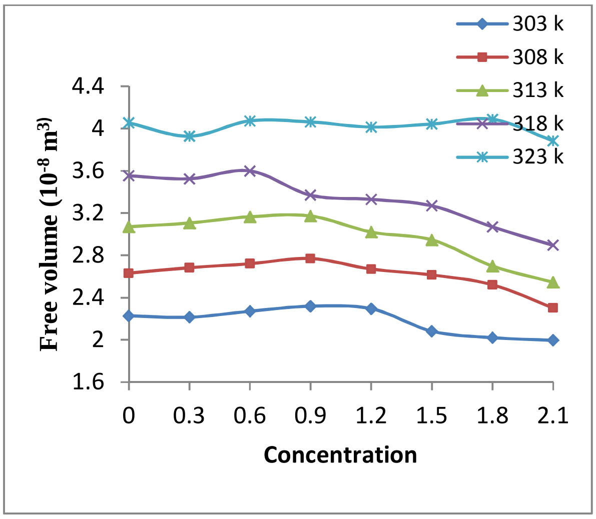

Fig .2 Concentration Vs Free volume

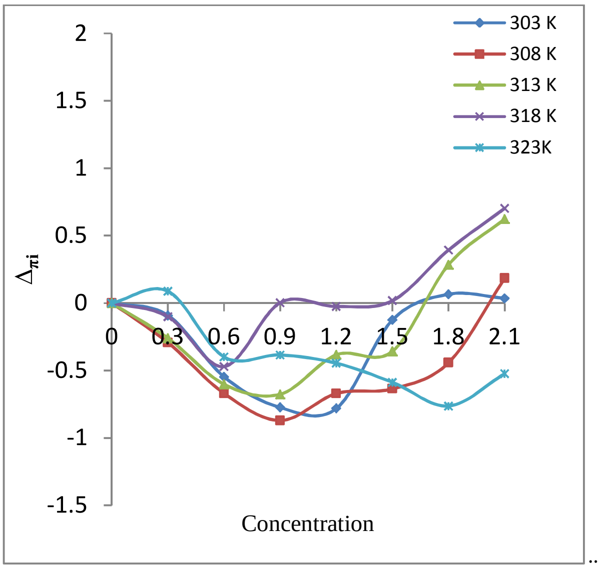

Fig 3. Concentration Vs $\Delta\pi_i$

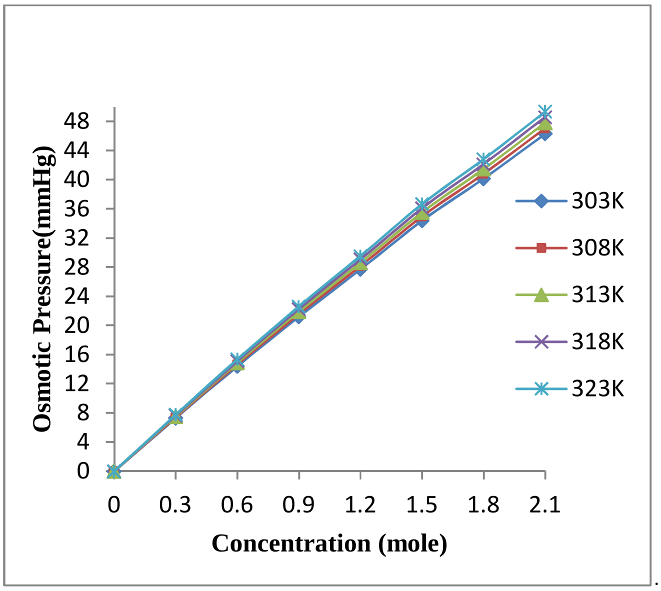

Fig. 4 Concentration Vs Osmotic pressure

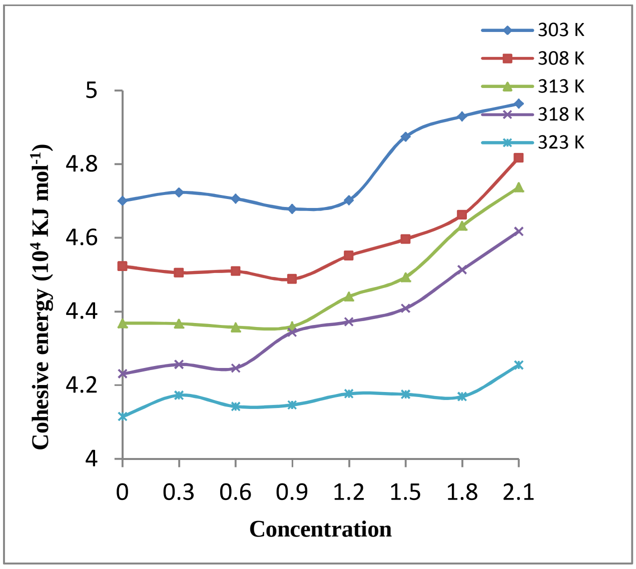

Fig. 5 Concentration Vs Cohesive energy

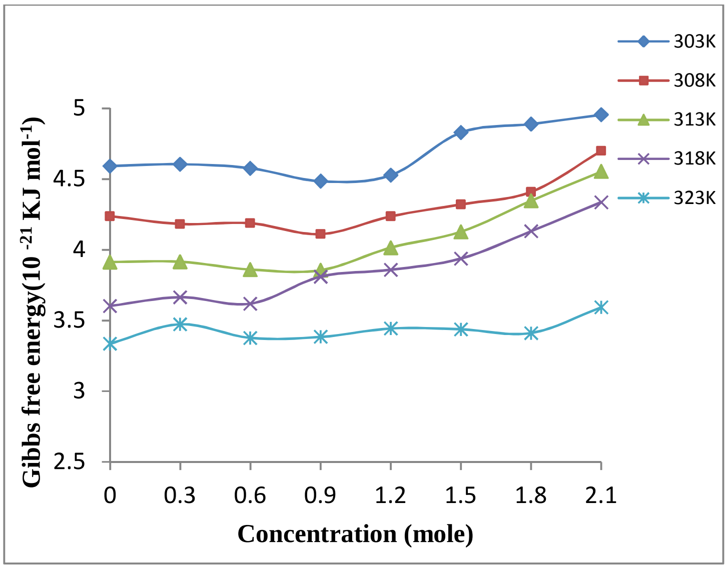

Fig. 6. Concentration Vs Gibb's free energy

CONCLUSION

Internal pressure, free volume and other related parameters are determined from the measured values of density, viscosity and velocity of aqueous solutions of urea. The variation of thermo dynamical parameters with molality of urea provides useful information about the nature of intermolecular interactions existing in the solutions. This investigation suggests that the structure breaking nature of urea in the bulk of solvent molecules is noted at lower concentrations. $\Delta\pi_i$ has been evaluated which gives an idea about the effect of cohesive forces in ion-solvent interaction. From the values of $\Delta\pi_i$ it is found that urea when added to water acts as a water-structure breaker.

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