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EXPLICATION OF MECHANICAL, THERMAL AND ELASTIC PROPERTIES OF UREA IN AQUEOUS MEDIA: AN ACOUSTICAL AND VOLUMETRIC APPROACH

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ABSTRACT:
The ultrasonic characterization helps to measure the speed of sound in pure as well as in mixture of liquids. Using the obtained experimental data of speed of sound and density, various properties like, mechanical, thermal and elastic of the liquid and liquid mixtures can be calculated. These properties are too useful in understating and gathering the knowledge of interaction between the solute and solvent components of liquid and their mixtures. In view from this scenario, present manuscript reports the investigation of urea in aqueous media to explore the intermolecular interaction in the liquid system (Urea+Water) at different concentration and temperaturesfor fixed 2MHz frequency. All mechanical, thermal and elastic parameter shows the positive values suggesting strong intermolecular interaction among ions of solute (urea) and water through hydrogen bonding. Thiskind of dataprovides the information require in many aspects and have applications in the field of agriculture, industries and pharmaceutical sectors.

Keywords :- Acoustic, elastic property, mechanical property, thermal property, volumetric.

INTRODUCTION :

Urea is highly active compound in a variety of biological functions in our body and has been referred as protein denaturing agent. Urea provides a significant role in the metabolism of compounds having nitrogen by animals and the light amount of substance contain nitrogen. Further urea is one of the essential basic materials for the chemical industry as well as in fertilizers for agriculture. Knowledge of thermodynamic and acoustical properties is of great importance in studying the physico-chemical behavior and molecular interaction between various essential molecules in a living organism and plants are very important.

The number of thermo-acoustical parameters are computed from the experimentally determine values of ultrasonic velocity (U) and density (ρ). Such studies as a function of concentration and temperature are useful in gaining insight into the structure and bonding of associated molecular compounds and other molecular processes. Though a number of investigations were carried out in mixture having Urea as one of the components at a constant frequency are reported.[1-4] Thus for clear observations, we report in this paper, the effect of urea on water, we study the various parameters of molecular interaction in aqueous urea solutions through ultrasonic measurements.

The ultrasonic sound velocity (U) and density (ρ) measurements[5-6] and their aligned properties (elastic, mechanical and thermal) find the wide applications in characterizing the physico-chemical behavior of liquid mixture.

Experimental Details

AR grade Urea (purity >>99.8%) having molecular weight: 60.06 g/mol and CAS number: 57-13-6, was obtained from Himedia Lab. Pvt. Ltd., Mumbai. Chemicals were used without further purification. The concentration of Urea in water was changed by weight.

Ultrasonic sound velocity in liquid mixture was measured by single crystal interferometer

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operating at frequency 2 MHz. The source of ultrasonic waves was a quartz crystal excited by a radio frequency oscillator placed at the bottom of a double jacketed metallic cylinder container. The cell was filled with the desired solution and water at constant temperature was circulated in the outer jacket. The cell was allowed to equilibrate for 30min. prior to making the measurements.The densities of the solutions were determined accurately using 10ml specific gravity bottle and electronic balance. The experimental temperature was maintained constant by circulating water with the help of automatic thermostatic water bath.

Defining Parameters

For the derivation of several elastic, mechanical and thermal properties the following defining relations reported in the literature are used:

(I) Surface Tension (σ): Surface tension is the tendency of liquid surface at rest to shrink into the minimum surface area possible = $(6.3*10^{-4})\rho U^{3/2}$

(II) Internal Pressure (πi): Internal Pressure is a significant parameter which is used to understand structure and nature of intermolecular interaction in the liquid molecules = $\{T\alpha/k_T\}$

(III) Isothermal Compressibility (k_T): Isothermal compressibility is used to determine the compressible properties of water supply.

a. Mc'Gowan Method (k_{T1}) = $1.33*10^{-8}/(6.4*10^{-4}U^{3/2}\rho)^{3/2}$

b. Pandey et al. Method (k_{T2}) = $17.1*10^{-4}/(T^{4/9}U^2\rho^{1/3})$

(IV) Bulk Modulus (K): Bulk modulus is the reciprocal of adiabatic compressibility; it is used to measure the ability of substance = $\frac{1}{\beta}$

(V) Thermal Conductivity (k): Thermal conductivity is referring to the ability of material or substance to conduct or transfer heat = $\{3.0*(\rho N_A/M)^{2/3}k_B U\}$

Isothermal Compressibility values have been computed using the McGowan's [7]Expression, using the arbitrary constant in the denominator of McGowan's expression by a temperature term. Pandey et al. [8]suggested a relation for the evaluation of isothermal compressibility.

RESULT AND DISCUSSION :

The ultrasonic velocity (U) of an aqueous solution of urea increases with an increase in concentration is shown in *Fig. 1*. The increase in sound speed is accredited to the cohesion/aggregation brought about by the ionic hydration and the construction of hydrogen bonds between the urea-water. The increase in ultrasonic velocity with rise in concentration for the present system confirms the greater molecular association. Urea (H_2N-CO-NH_2) molecules contain –NH_2, -CO groups which are hydrophilic groups. So interaction between solute and water molecules complete through hydrophilic hydration. As the temperature is increased several water molecules from the hydration co-sphere relaxes.[9] This result in more and more number of monomeric water molecules. These forms closed packed structure and behaves as a stiff material medium for the propagation of ultrasonic wave. Hence ultrasonic velocity increases with rise in temperature.

The density (ρ) of the aqueous urea (as shown in Fig. 2), increases with increase in concentration due to the association occurs between solute and solvent molecules. The increase in density increases the molar volume indicating the association in the components of the constituent molecules and confirms the structural rearrangement. Furthermore, density decrease with rise in temperature shows decrease in intermolecular forces due to increasing thermal energy of the system.[10]

Surface tension is used to study the surface composition of aqueous solution of the mixture. The increasing trend of surface tension (σ) as shown in *Fig. 3* with concentration of solute indicates that the significantassociation in the

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solution.[11]As we know that the acoustical parameters have tendency to explain the ilk and strength of the interaction taking place in the solutions.[12] In the present system the internal pressure (π_i) increases with increase in concentration of fertilizer at all the temperatures as shown in *Fig. 4*. This behavior of the solution indicates the intermolecular space decreases with addition of fertilizer in water and interaction increases which supports the association among the constituent molecules of the solute and solvent.[13]

The overall trends in the isothermal compressibility ($k_{T1}$and k_{T2}) are as shown in *Fig. 5* and *Fig.6*. It has been found to be decreasing with increase in concentration. The decrease in 'k_T' values with increase in concentration seems to be the result of corresponding decrease in free volume.[14] The decrease in free volume with rise in concentration clears the clustering of molecules and hence suggest the increase in interaction.

The mechanical properties of any kind of liquid can be understood by bulk modulus (K), as the hydrogen bonding between the unlike components in the solutions increases with the bulk modulus. In the present case it is found that the bulk modulus increases with increase in concentration. Because, as water is polar solvent and when urea mixed, the well intermolecular interaction occurred, resulting in close packing of molecules. The increase values of bulk modulus shown in *Fig. 7*, Indicate the strong association of urea and water molecules. Further, with the increase of temperature the mean distance between the molecules tend to increase with a corresponding increase in bulk modulus.

The thermal conductivity (k) of a pure liquid (solvent) and solution were calculated by using Bridgman's relation.[15,16] As Ultrasonic velocity determination or measurement can be utilized to evaluate thermal conductivity theoretically. The theoretical value of thermal conductivity of solvent (water) shows good agreement with the literature data. From *Fig. 8* it is observed that the evaluated value of thermal conductivity for Urea is more than that of the water at all concentrations and temperature. In the current investigation, both the ultrasonic velocity and density values increases with increase in temperature and as per Bridgeman's relation, thermal conductivity is directly depends on these two factors.[17] The increase in thermal conductivity with increase in concentration and temperature clear that the flow of energy is possible when molecules get close to each other. This means in present system intermolecular interaction taking place. It is confirm with rise of velocity, density and drop of free length values due to close packing structure.

CONCLUSION :

In the light of above observations and discussions, it may be concluded that:

❖ The concentration, nature of solute, nature of solvent and its position plays an important role in determining the interactions occurring in the solution.

❖ From the acoustical and thermo-dynamical parameters it is concluded that H-bonding interaction is strong at higher concentration.

❖ The thermo-acoustic and physico-chemical parameters exhibit the strength of molecular interaction.

❖ Ultrasonic and volumetric measurements were carried out on aqueous urea for various concentrations (0.02-0.2 mol-kg^{-1}) at all temperatures. In the light of above experimental values of ultrasonic velocity, density and their allied elastic property, mechanical property and thermal property, it may be concluded that there exist of solute-solvent interaction in the present system.

The possibility of intermolecular H-Bonding in the solution represented in following *Fig. 9.*

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Table: The values of Ultrasonic Velocity (U), Density (ρ), Surface Tension (σ), Internal Pressure (πi), Isothermal Compressibility's (k_{T1} and k_{T2}), Bulk Modulus (K) and Thermal Conductivity (k) of aqueous Urea at 288.15 and 293.15K temperature

Conc. ($mol\text{-}kg^{-1}$)	U	ρ	σ	$\pi i*10^{+9}$	$(kT_1)*10^{-12}$	$(kT_2)*10^{-12}$	$K*10^{10}$	k
	ms^{-1}	Kgm^{-3}	Nm^{-1}	Nm^{-2}	m^2N^{-1}	m^2N^{-1}	$m^{-2}N$	$Wm^{-1}K^{-1}$
	T=288.15K							
0.00	1466.032	999.103	35331.82	4.90	61.85	64.22	0.214735	0.629185
0.02	1468.302	999.506	35428.20	4.92	61.60	64.01	0.215485	0.629976
0.04	1469.024	1000.127	35476.36	4.93	61.47	63.94	0.215829	0.630194
0.06	1470.133	1000.649	35535.08	4.94	61.32	63.83	0.216268	0.630537
0.08	1471.764	1001.050	35608.49	4.95	61.13	63.68	0.216835	0.631053
0.10	1472.245	1001.907	35656.45	4.96	61.01	63.62	0.217165	0.631268
0.12	1472.914	1002.463	35700.56	4.97	60.89	63.55	0.217481	0.631438
0.14	1473.333	1002.988	35734.50	4.97	60.81	63.35	0.217718	0.631487
0.16	1474.432	1003.649	35798.06	4.98	60.65	63.34	0.218188	0.631886
0.18	1475.642	1004.418	35869.60	4.99	60.46	63.25	0.218713	0.632378
0.20	1477.239	1005.121	35952.99	5.01	60.25	63.12	0.219342	0.633008
	T=293.15K							
0.00	1481.496	998.200	35859.88	5.06	60.49	62.43	0.219087	0.635439
0.02	1482.238	998.926	35912.92	5.07	60.36	62.35	0.219467	0.635709
0.04	1482.922	999.6242	35962.91	5.08	60.23	62.28	0.219824	0.635943
0.06	1483.522	1000.424	36013.53	5.09	60.10	62.21	0.220177	0.636184
0.08	1484.238	1000.859	36055.27	5.10	60.00	62.14	0.220420	0.636321
0.10	1484.892	1001.568	36104.66	5.11	59.88	62.07	0.220838	0.636548
0.12	1485.385	1002.307	36149.33	5.12	59.77	62.02	0.221259	0.636718
0.14	1485.955	1002.813	36188.37	5.12	59.67	61.96	0.221425	0.636823
0.16	1488.238	1002.965	36277.30	5.14	59.45	61.76	0.222143	0.637513
0.18	1489.382	1003.461	36337.09	5.15	59.30	61.66	0.222593	0.637860
0.20	1491.101	1003.795	36412.14	5.16	59.12	61.51	0.223184	0.638386

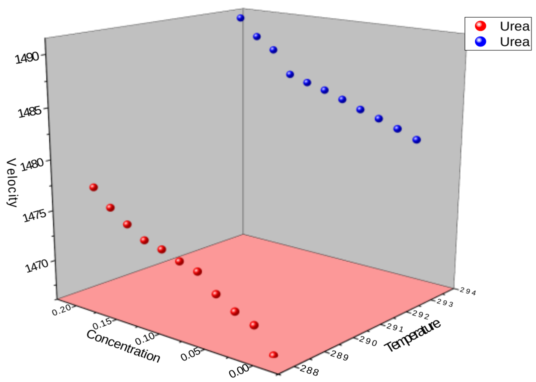

Fig.1: Variation of Ultrasonic velocity with Temperature and Concentration.

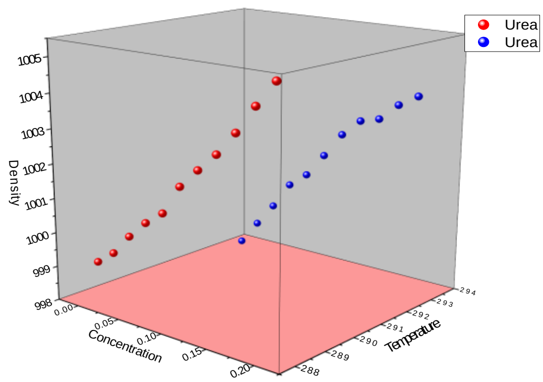

Fig.2: Variation of Density with Temperature and Concentration.

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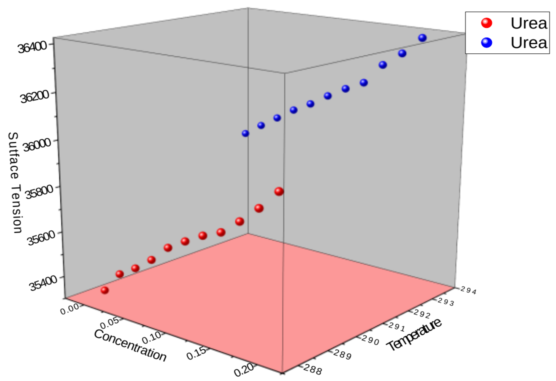

Fig.3: Variation of Surface Tension with Temperature and Concentration.

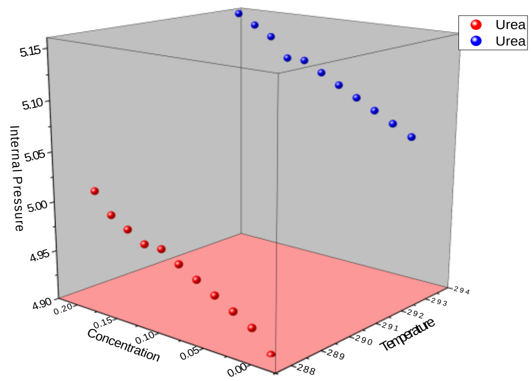

Fig.4: Variation of Internal Pressure with Temperature and Concentration.

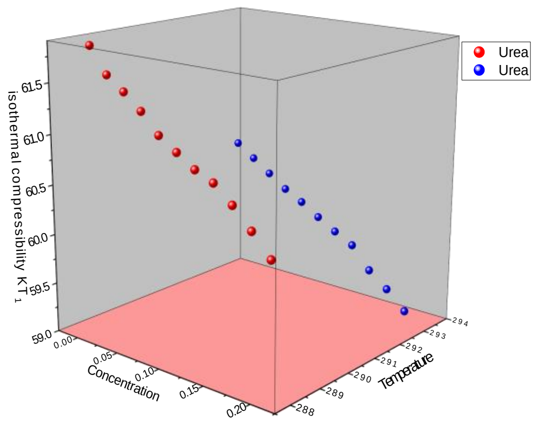

Fig.5: Variation of Isothermal Compressibility-1 with Temperature and Concentration.

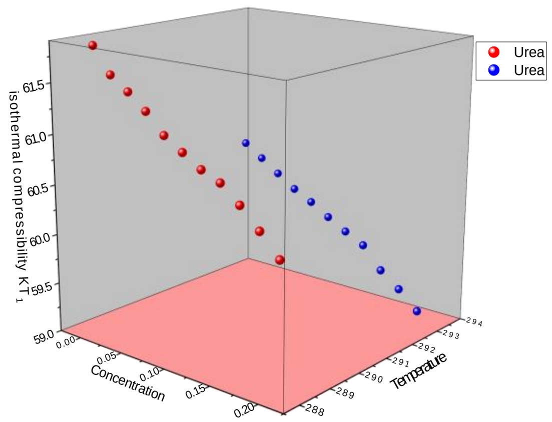

Fig.6: Variation of Isothermal Compressibility-2 with Temperature and Concentration.

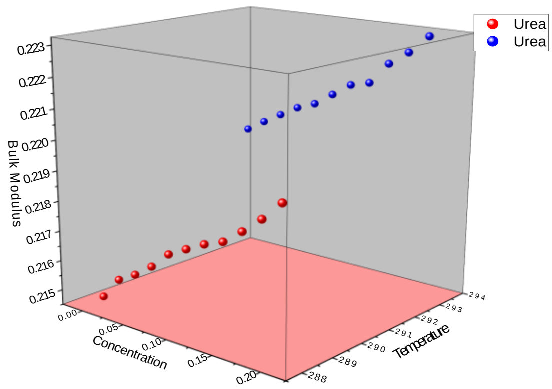

Fig.7: Variation of Bulk Modulus with Temperature and Concentration.

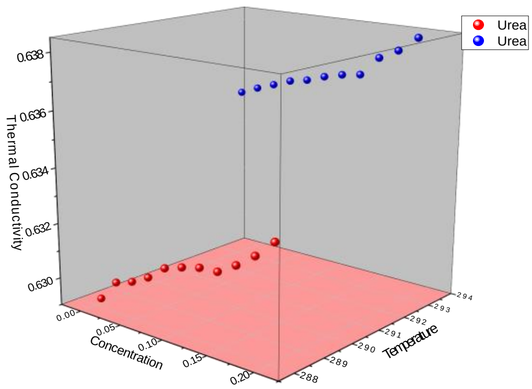

Fig.8: Variation of Thermal Conductivity with Temperature and Concentration.

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