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Study of Acoustical and Thermodynamic Properties of Aqueous Solution of NaCl at different Concentrations and Temperatures through Ultrasonic Technique

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ABSTRACT

The Ultrasonic velocity, density, and viscosity have been measured for aqueous solution of NaCl at different concentrations, at different temperatures and at constant frequency (9 MHz). These experimental data have been used to estimate the thermodynamic parameters such as adiabatic compressibility, free length, internal pressure, relaxation time, acoustic impedance, and Gibb's free energy for the solution. This kind of study is important for both humans as well as plants.

Key Words: Ultrasonic velocity, Acoustical and thermodynamical properties.

INTRODUCTION

Ultrasonic is a versatile non-destructive technique and highly useful for investigation of various physiochemical properties such as Adiabatic compressibility, intermolecular free length, internal pressure, relaxation time, Gibb's free energy of solution at different temperatures.

Recent developments have found use of ultrasonic energy in medicine, engineering and agriculture [1-3]. Ultrasonic study on the amino acids with aqueous solution of electrolytes and non-electrolytes provides useful information in understanding the behavior of liquid systems. Electrolytes are also known to influence the stability of biological molecules such as proteins. Ultrasonic studies have also been made for simple carbohydrates in water [4-5]. Frank and Kalgud have also used the same method to study the thermodynamic properties of several carbohydrates like ribose, galactose etc [6]. We know that sodium, potassium level in human blood is of considerable importance for several reasons, Sodium maintains the normal distribution of water and the osmotic pressure in the various fluid components. Potassium influences the acid base balance and osmotic pressure including water retention. Increased sodium levels are found in severe dehydration. Decreased levels are found in sever poly-urea, metabolic acidosis, diarrhea and renal insufficiency. This Sodium and potassium levels in serum have been studied by various methods such as Ion-exchange method, Chemi Luminescence immune assay (CLIA), Chromatography etc [7]. Further osmosis is also of considerable importance in biological systems. Ultrasonic study of variation of different parameters with concentration may lead to change in the osmotic flow. Osmotic flow is also temperature dependent.

Since sodium salt is important to humans as well as plants, we have done ultrasonic study of NaCl solution of different concentration at different temperatures and at a particular frequency. The nature of variation in different parameters has been analysed with respect to concentration of NaCl. To our knowledge, these measurements at different temperatures have not been made so far.

MATERIALS AND METHODS

Experimental Details

Fresh distilled water has been used as solvent for preparing sodium chloride (NaCl) solutions of different concentration. Sodium chloride used as solute for the solution is of analytical reagent (AR) grade, manufactured by reputed firm E-Merk Ltd. (India).

(i) Velocity Measurement:-

The velocity of ultrasonic wave in the NaCl solutions (Molality- 0.8562, 1.711, 2.566, 3.422) have been measured using multi-frequency ultrasonic interferometer with an high degree of accuracy operating at 11 different frequencies (Model M-84) supplied by M/s Mittal Enterprises, New Delhi. The measuring cell of interferometer is a specially designed double walled vessel with provision for temperature constancy. An electronically operated digital constant temperature bath (Model SSI-03spl) supplied by M/s Mittal Enterprises, New Delhi, operating in the temperature range -10^{o}c to 85^{o}c with an accuracy of ± 0.1K has been used to circulate water through the outer jacket of the double walled measuring cell containing the experimental liquid.

(ii) Density Measurement:-

The densities of solutions are measured using a 25ml specific gravity bottle. The specific gravity bottle with the experimental liquid is immersed in a temperature controlled water bath. The density was measured using the formula

$$\rho_2 = (w_2/w_1).\ \rho_1$$

Where, W_1 = weight of distilled water, W_2 = Weight of experimental liquid, ρ_1 = Density of water, ρ_2 = Density of experimental liquid

(iii) Viscosity measurement:-

The viscosities of solution are measured using an Oswald's viscometer calibrated with double distilled water. The Oswald's viscometer with the experimental liquid is immersed in a temperature controlled water bath. The time of flow was measured using a racer stop watch with an accuracy of 0.1 sec. The viscosity was determined using the relation,

$$\eta_2 = \eta_1\ (t_2/t_1)\ (\rho_2/\rho_1)$$

Where, $\eta 1$ = Viscosity of water, η_2 = Viscosity of experimental liquid, ρ_1 = Density of water, ρ_2 = Density of experimental liquid, t_1 = Time of flow of water, t_2 = Time of flow of experimental liquid.

Theoretical Aspect

The following thermodynamic parameters were calculated from Jacobson's relation [8-10].

(i) Adiabatic Compressibility (β):-

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. It is calculated from the speed of sound and the density (ρ) of the medium by using the equation of Newton Laplace as

$$\beta = 1/U^{2}\cdot\rho$$

(ii) Intermolecular free length (L_f) :-

The intermolecular free length is the distance between the surfaces of the neighboring molecules. It is calculated by using the relation

$$L_f = K_T\beta^{1/2}$$

Where K_T is the temperature dependent constant.

(iii) Internal Pressure (π_i):-

The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant o force of attraction and force of repulsion between the molecules. It is calculated by using the relation,

$$\Pi_i = bRT\,(k\eta/U)^{1/2}\,(\rho^{2/3}/M^{7/6})$$

Where, 'b' stands for cubic packing, which is assumed to be '2' for all liquids, ' K ' is a dimensionless constant independent of temperature and nature of liquids. Its value is 4.281 x 10^9. 'T' is the absolute temperature in Kelvin, 'M' is the effective molecular weight, 'R' is the Universal gas constant, 'η' is the viscosity of solution in $N.S.m^{-2}$, 'U' is the ultrasonic velocity in $m.s^{-1}$ and 'ρ' is the density in $Kg.m^{-3}$ of solution.

Table 1: Values of density (ρ), viscosity (η) and Ultrasonic velocity (U) at 289K, 293K, 303K and 313 K

Molality mol /Kg	T kelvien	$\rho \times 10^3$ $kg.m^{-3}$	$\eta \times 10^3$ $N.s.m^{-2}$	V $m.s^{-1}$
0.8562	283	1.0435	1.38	1535.36
	293	1.0405	1.0532	1560.52
	303	1.0364	0.8463	1580.25
	313	1.0354	0.71	1590.23
1.711	283	1.078	1.44	1563.75
	293	1.075	1.0973	1590.3
	303	1.071	0.87705	1606.05
	313	1.067	0.73	1615.2
2.566	283	1.120	1.52	1609.6
	293	1.116	1.13858	1624.5
	303	1.111	0.8989	1641.15
	313	1.106	0.74	1656
3.422	283	1.163	1.58	1653
	293	1.158	1.17981	1665
	303	1.153	0.92985	1672.8
	313	1.148	0.76	1692.6

Table 2: Values of Adiabatic compressibility (β), Free length (L_f), Relaxation time (τ), Acoustic impedance (Z) and Gibb's free energy (ΔG) at 283K, 293K, 303K and 313K.

Molality mol /Kg	T kelvien	$\beta \times 10^{-10}$ $m^2.N^{-1}$	$\tau \times 10^{-10}$ Sec.	$L_f \times 10^{-8}$ m.	$\pi_i \times 10^4$ $N.m^{-2}$	$Z \times 10^4$ $Kg.m^{-2}.s^{-1}$	$\Delta G \times 10^{-20}$ $K.J.mol^{-1}$
0.8562	283	4.0649	7.48	1.232	448.3749	160.2271	3.2788
	293	3.9465	5.54	1.234	401.4776	162.3768	3.2875
	303	3.8637	4.36	1.24	368.8734	163.7850	3.3133
	313	3.8191	3.62	1.255	347.6891	164.6556	3.3558
1.711	283	3.791	7.28	1.19	470.923	168.6878	3.2682
	293	3.6765	5.38	1.191	421.192	171.0333	3.2754
	303	3.6177	4.23	1.2	386.5684	172.1095	3.3007
	313	3.5917	3.5	1.217	362.2835	172.3764	3.3413
2.566	283	3.4455	6.98	1.134	495.4164	180.3119	3.2520
	293	3.3947	5.15	1.144	440.8426	181.3364	3.2581
	303	3.3394	4	1.153	401.9459	182.4688	3.2775
	313	3.2944	3.25	1.165	373.9212	183.2990	3.3098
3.422	283	3.1458	6.63	1.084	516.6142	192.3070	3.2316
	293	3.1129	4.9	1.096	459.3138	192.9384	3.2374
	303	3.0972	3.84	1.11	419.4915	193.0100	3.2602
	313	3.0397	3.08	1.119	388.2248	194.3609	3.2866

(iv) Relaxation time (τ):-

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and impurities. The relaxation time can be calculated from the relation,

$$\tau = 4/3.\ (\beta.\eta)$$

(v) Acoustic impedance (Z):-

The specific acoustic impedance is given by,

$$Z = U.\rho$$

Where 'U' and 'ρ' are velocity and density of NaCl solution.

(vi) Gibb's free energy:-

The Gibb's free energy is calculated by using the relation

$\Delta G = KT.Ln\ (KT\tau/h)$

Where, τ is the viscous relaxation time, 'T' is the absolute temperature, 'k' is the Boltzmann's constant and 'h' is the Planck's constant.

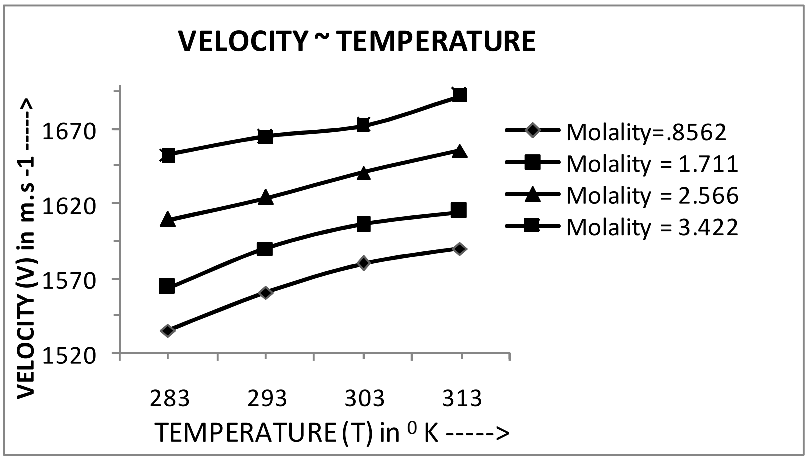

Fig-1: Variation of ultrasonic velocity with temperature.

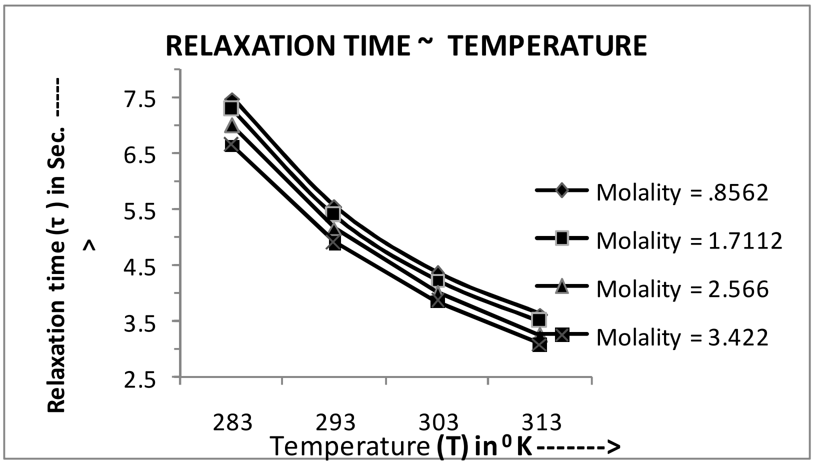

Fig-2: Variation of Relaxation time with temperature

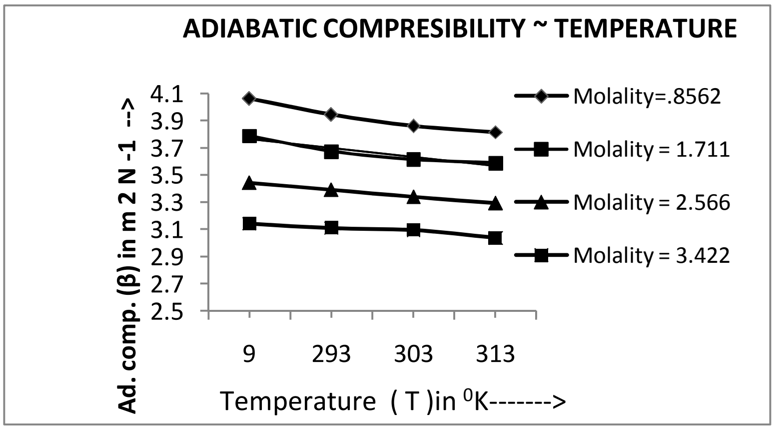

Fig-3: Variation of adiabatic compressibility with temperature

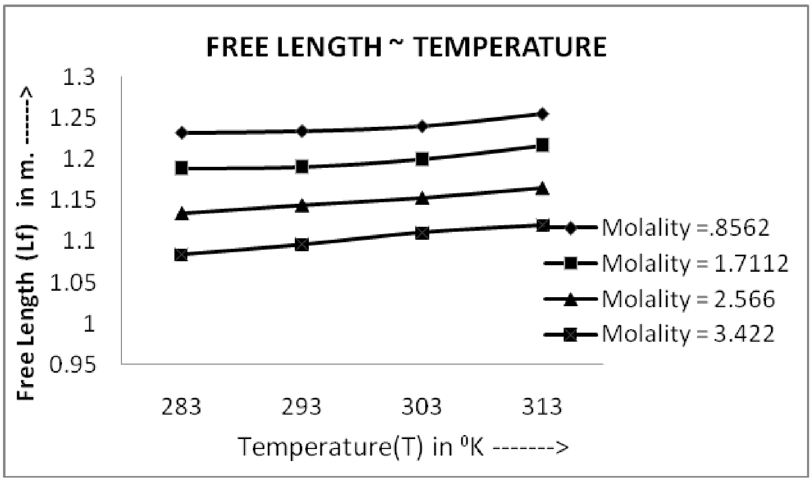

Fig-4: Variation of free length with temperature

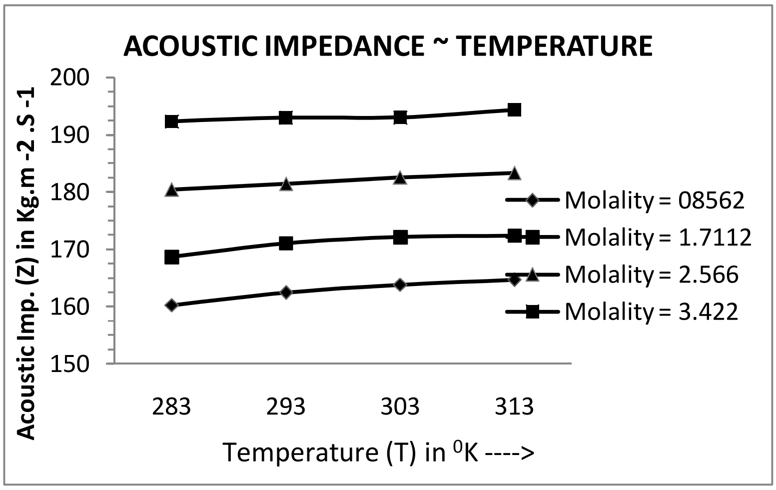

Fig-5: Variation of acoustic impedance with temperature

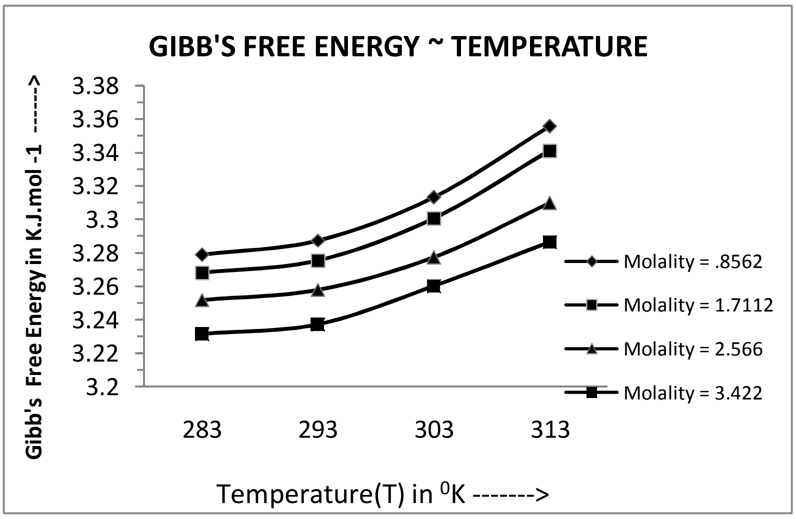

Fig-6: Variation of Gibb's free energy with temperature

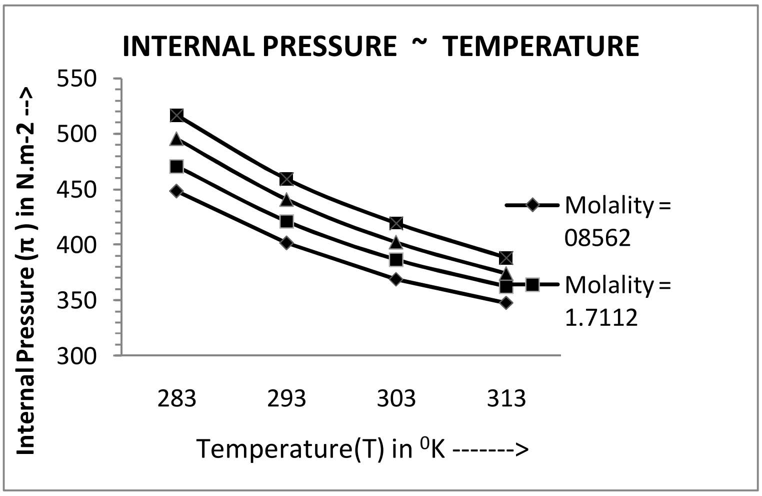

Fig-7: Variation of internal pressure with temperature

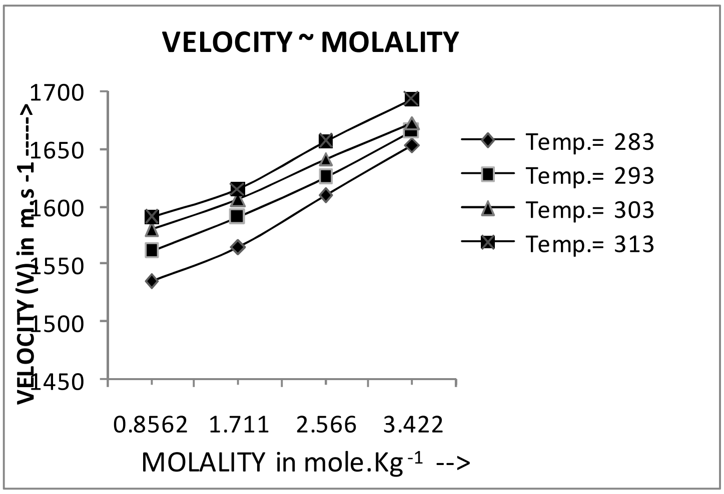

Fig-8: Variation of ultrasonic velocity with molality

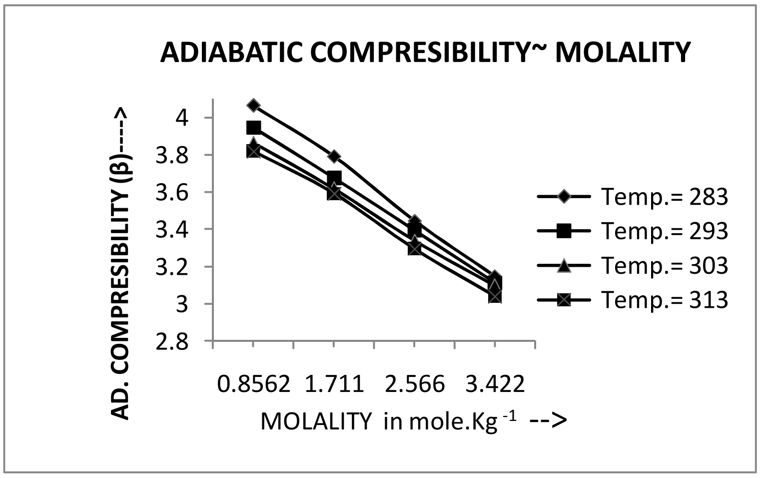

Fig-9: Variation of adiabatic compressibility with molality

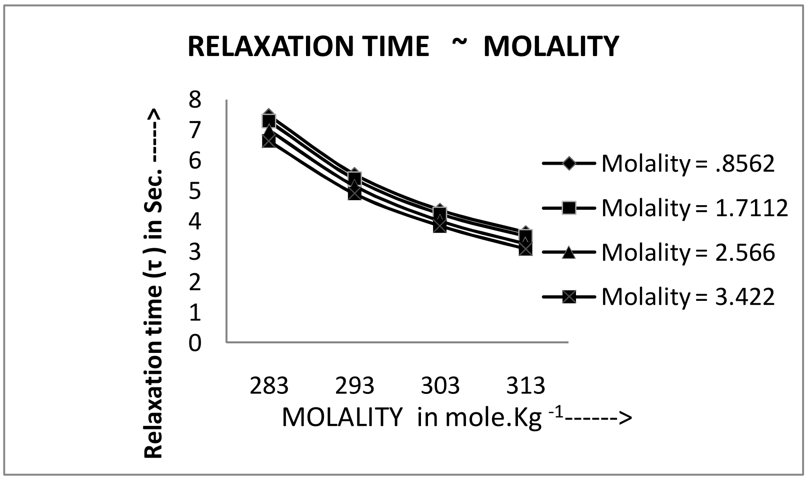

Fig-10: Variation of relaxation time with molality

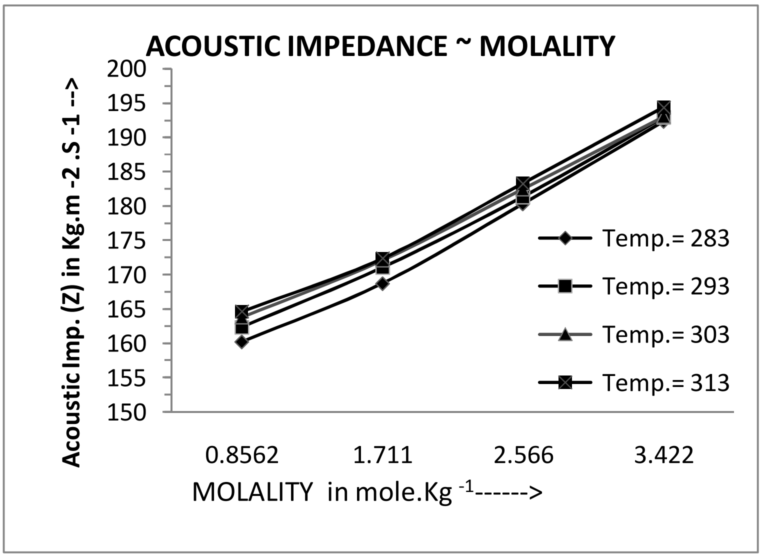

Fig-11: Variation of acoustic impedance with molality

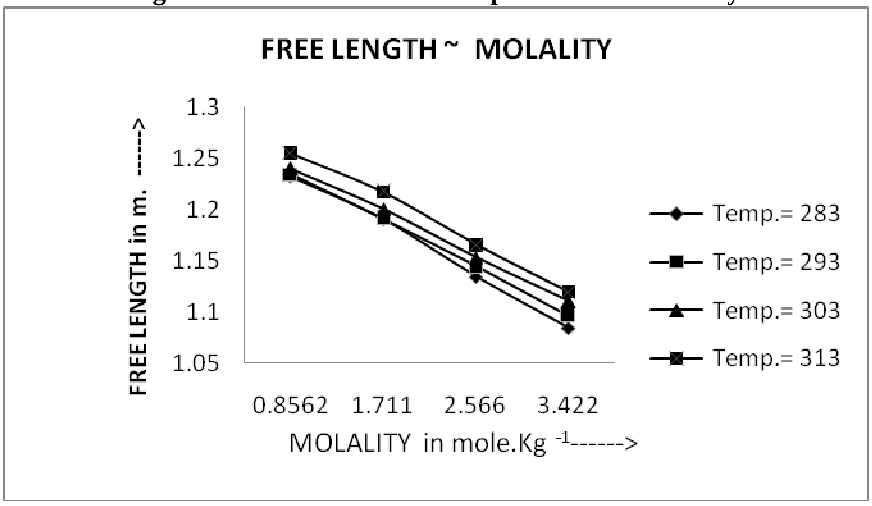

Fig-12: Variation of free length with molality

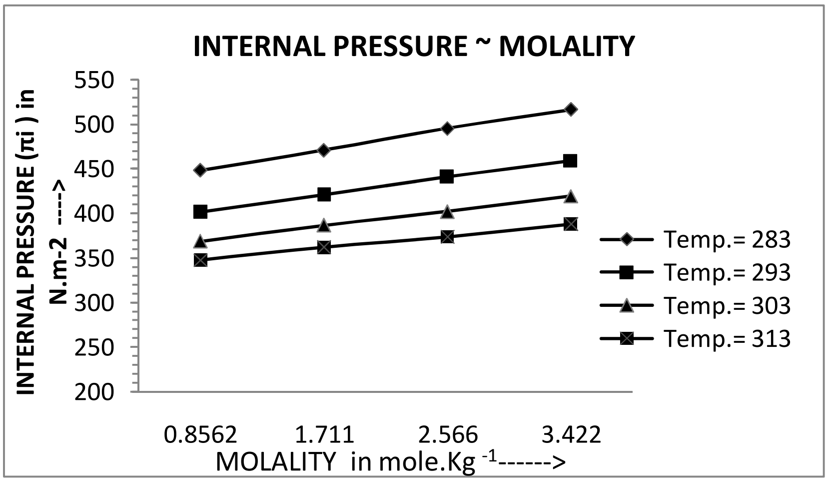

Fig-13: Variation of internal pressure with molality

RESULTS

The Ultrasonic velocity, density and viscosity of aqueous solution of NaCl of different concentrations are presented in table-1 at temperatures 283K, 293K, 303K, 313 K. Density and viscosity decreases with increase in temperature, where as velocity increases.

Thermodynamic parameters such as adiabatic compressibility (β), free length(L_f), internal pressure (π_i), relaxation time (τ), acoustic impedance (Z), and Gibb's free energy (ΔG) of the solution are calculated and listed in Table-2.

The variations of the different parameters with temperature as well as concentration of NaCl have been plotted [Fig 1 to 13].

Adiabatic compressibility, relaxation time and internal pressure decrease with increases in temperature whereas free length, acoustic impedance and Gibb's free energy increases with increase in temperature.

Density, viscosity, velocity, acoustic impedance and internal pressure increase with concentration whereas adiabatic compressibility, relaxation time, free length and Gibb's free energy decrease with concentration.

DISCUSSION

The decrease in density and viscosity with increase in temperature indicates decrease in intermolecular forces due to increase in thermal energy of the system. This causes an expansion in volume and hence increases in free length.

The H- bonded structure of water is disrupted by the addition of NaCl. The electrolytes occupy the interstitial space of water and tend to break the original ordered state of water. Interaction between solute and solvent molecules results in decrease in free length and increase in density, viscosity and velocity with increase of solute concentration at all temperatures.

With increase in temperature there occurs a structural rearrangement as well as a result of hydration leading to a comparatively more ordered state. Therefore ultrasound speed increases with increase in temperature.

Adiabatic compressibility decreases with increase in concentration. A large portion of the water molecule exerts electrostatic force which attracts the neighboring molecules decreasing the effective volume of water. This leads to the decrease in compressibility.

Gibb's free energy decreases with concentration. It is observed that decrease in free energy favours the formation of products after reaction.

The viscous relaxation time shows the presence of molecular interaction due to addition of solute and the same is confirmed by Gibb's free energy parameters. As expected, internal pressure decreases with increase of temperature and increases with increase of concentration.

CONCLUSION

Ultrasonic method is a powerful probe for characterising the physio-chemical properties of liquids. This method has been used to study the above properties of aqueous solution of NaCl, being an essential part of the biological system.

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