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ACOUSTICAL STUDY OF SUBSTITUTED THIAZOLES IN NNDMF – WATER MIXTURES AT DIFFERENT TEMPERATURES

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Abstract:
Density, ultrasonic velocity of pure solvent N,N-dimethylformamide (NNDMF) and ligand solutions of substituted thiazoles in 70% NNDMF-water mixture were measured at different temperatures (303.15, 308.15, 313.15 and 318.15)K. Acoustical parameters such as adiabatic compressibility, intermolecular free length, acoustical impedance, apparent molar volume and relative association were determined from experimental data of density and ultrasonic velocity. The effect of temperature variations on the strength of molecular interaction has been studied. An excellent correlation represents in terms of solute-solvent and solvent-solvent interactions at all temperatures.
Keywords: density, ultrasonic velocity, acoustical parameter, molecular interaction, thiazole, NNDMF.

INTRODUCTION:

Thiazole and its derivatives are of biological significance[1-5] and study of the molecular interaction in the solution will be useful to understand their biological applications. Sulphur and nitrogen containing heterocyclic compounds represent an important class of drugs in the therapeutic chemistry and also contributed to the society from biological and industrial point which helps to understand life processes[6]. Ultrasonic technique is useful for the studies of physicochemical properties of a system. Study of molecular interaction in liquid provides valuable information regarding internal structure molecular association, complex formation, internal pressure etc. The studies of solution properties of liquid solution of polar as well as non polar components have great application in industrial and technological process[7]. The recent publication[8-13] in this area shows that the many researchers give attention towards study of ultrasonic velocity measurement and study of acoustical properties.

Different liquids flow with different rates flow of liquids depend upon nature of the molecules present in the substance and how easily they can slide over one another during their flow. Nagargun et al[14] have studied speeds of sound and density for binary mixtures of ethyl benzoate (EB) with N,N-dimethylformamide (NNDMF), N,N dimethylacetamide (NNDMAc) and N,N-dimethylaniline (NNDMA) as a function of mole fraction at different temperature and atmospheric pressure. Recently Rupali Talegaonkar et al[7] have been studied the acoustical properties of substituted thiazolyl schiff's base in binary solvent mixture at fixed temperature. Naik et al[15] reported the molecular interactions in substituted pyrimidins-acetonitrile solutions at different temperature. Measurement of ultrasonic study of an organic ligands solutions provide an excellent method of obtaining data on the ion solvent and solvent-solvent interaction and structure breaking and making properties of solutes. The ultrasonic velocities, densities and relative association of substituted thiazoles used in this investigation in polar aprotic-polar protic mixed media at different temperature was lacking and therefore the present work is undertaken to study sound velocities and densities of these thiazoles of 0.01 mol/dm^3 concentrations in 70:30 (v/v) NNDMF-water mixture at different temperature in order to know effect of temperatures on various acoustical properties. The applications of these thiazoles in different field of science developed our interest in the measurement of their velocities and densities and compute the acoustical properties to understand their interaction with non aqueous solvent mixture at different temperature.

MATERIALS AND EXPERIMENTAL:

The solvent N, N-dimethylformamide (NNDMF) of Analytical grade used without purification. The ligands 2-mercaptobenzothiazole(L_1), 2-amino-5-methylthiazole(L_2), 2-amino-5-nitrothiazole(L_3), 2-chlorobenzothiazole(L_4) and Benzothiazole(L_5) were obtained from Hi-MEDIA. The ligand solutions were prepared by dissolving an accurate amount in an organic-aqueous mixture in standard flask with airtight caps and the mass measurement were performed using high precision digital balance (Adair Datta of accuracy ±0.01 mg). The ultrasonic velocities of pure component and their mixtures were measured by ultrasonic interferometer (Mittal enterprises, model F-81s) at 2 MHz with frequency tolerance ± 0.03 %. It consists of high frequency generator and a measuring cell. The densities of NNDMF and ligand solutions were measured by digital density meter (Anton Paar DMA 35).

THEORY:

Numerous methods are available in the literature for measuring ultrasonic velocity in solid and liquids. The ultrasonic interferometer is considered as more reliable and precise instrument. The expression used to determine ultrasonic velocity using ultrasonic interferometer is;

$$u = \upsilon\lambda$$

Where u is ultrasonic velocity and λ is wavelength.

The adiabatic compressibility (β_s) was calculated from following equation;

$$\beta_s = 1/\rho_s u^2$$

Where ρ_s is density of solution and u is speed of ultrasonic velocity.

Intermolecular force is one way or another way to determine the properties of liquids of attractive and repulsive forces. The intermolecular free length (L_f) is calculated by using the standard expression;

$$L_f = K \beta_s^{1/2}$$

Where K is temperature dependent constant known as a Jacobson constant[16].

The acoustic impedance (Z) is obtained by equation;

$$Z = u\rho$$

The relative association (R_A) was calculated by the following equation;

$$R_A = (\rho_s/\rho_o)(u_o/u_s)^{1/3}$$

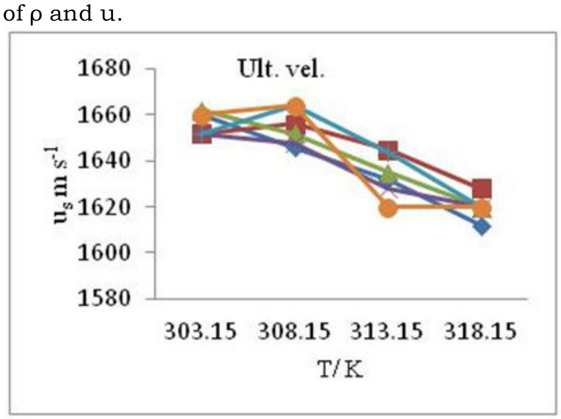
Where ρ_o is density of solvent and u_o is velocity of solvent. Also the apparent molar volume is calculated by from following equation;

$$\phi_V = (1000/m\rho_s\rho_o) - (\rho_0 - \rho_s) + (M/\rho_0)$$

ϕ_v is apparent molar volume; M is molar mass of the solute.

RESULTS AND DISCUSSION:

The calibration of the ultrasonic interferometer was done by measuring the ultrasonic velocities and densities of the pure NNDMF and distilled water respectively. The measured value is found to be good concordance with literature values which are shown in table 1. Small difference may occur due to difference in purity of chemicals, measurements, techniques and calibrations. Figure 1 represents the temperature dependence of densities of solutions of NNDMF (pure solvent) and various ligands (solutes) having concentration 1×10^{-2}. The values of densities and ultrasonic velocities of L_1, L_2, L_3, L_4 and L_5 listed in table 2 and 3 respectively and the values of acoustical parameters such as adiabatic compressibility, relative association, acoustical impedance, apparent molar volume and linear free length listed in table 4. The fig 2 shows that ultrasonic velocity values decrease with increase of temperature due to the breaking of hetero-and homomolecular clusters at high temperatures[14]. The decrease of ultrasonic velocity and density with increase of temperature indicates that cohesive forces decreased[17]. The increasing temperature has two opposite effects namely increase of molecular interaction (structure formation) and destruction of structure formed previously. When the thermal energy is greater than the interaction energy, it causes the destruction of previously formed structure. Thus, the increase of temperature favors the increase of kinetic energy and volume expansion and hence, results in the decrease of ρ and u.



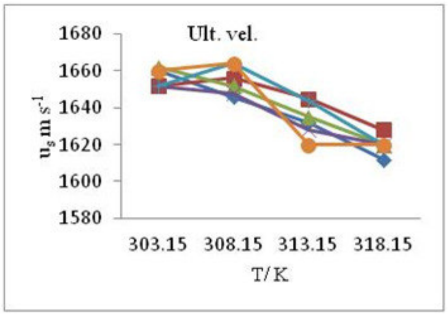


Figure 2:- . The temperature dependence of density in solutions of NNDMF--■-- ,NNDMF+L_1--♦--, NNDMF+L_2--▲--, NNDMF+L_3--×--, NNDMF+L_4--+- and NNDMF+L-●-- in NNDMF with concentration 1×10^{-2}.

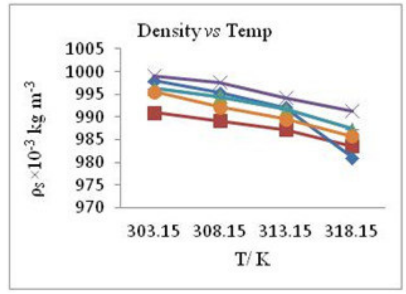


Figure 3. The temperature dependence of ultrasonic velocity in solutions of NNDMF--♦--, NNDMF+ L_1--■--, NNDMF+L_2--▲--, NNDMF+L_3--×-, NNDMF+L_4--+- and NNDMF+ L_5-●-- in NNDMF with concentration 1×10^{-2}

Table 1:- Experimental and literature values of density and ultrasonic velocity

		Expt.		Lit	
	T/ K	$\rho_0\times10^{-3}$,kg m^{-3}	u_0,ms^{-1}	$\rho_0\times10^{-3}$,kg m^{-3}	u_0,ms^{-1}
Distilled Water	303.15	996.5	1516	996[22]	1506 [23]
	308.15	994[15]	1520[15]		
NNDMF	303.15	991	1612	990.3[24]	1608[20]
	308.15	989.2	1632	990.3	
	313.15	987.3	1648		1633[21]

Table 2:- Experimental density of L_1, L_2, L_3, L_4 and L_5 in NNDMF at different temperatures with solute concentration 1×10^{-2} M

		ρ_s ,kg m^{-3}				
T/K	NNDMF	NNDMF+L_1	NNDMF+L_2	NNDMF+L_3	NNDMF+L_4	NNDMF+L_5
303.15	991	996.3	995.8	999.1	998.5	995.6
308.15	989.2	994.5	992.4	997.7	995.4	992.2
313.15	987.2	991.7	989.2	994.3	992.1	989.5
318.15	983.6	987.4	986.2	991.4	989.1	985.8

Table 3.Experimental ultrasonic velocities of L_1, L_2, L_3, L_4 and L_5 in NNDMF at different temperatures with solute concentration 1×10^{-2} M

		u_s, m s^{-1}				
T/K	NNDMF	NNDMF+L_1	NNDMF+L_2	NNDMF+L_3	NNDMF+L_4	NNDMF+L_5
303.15	1660	1652	1662	1652	1652	1660
308.15	1646	1656	1652	1648	1664	1664
313.15	1632	1645	1635	1628	1648	1620
318.15	1612	1628	1620	1620	1620	1620

When ultrasonic waves incident on the solution, the molecules get perturbed. The reason is medium has some elasticity and due to this perturbed molecules regain their equilibrium positions[17]. When a solute is added to a solvent, its molecules attract certain solvent molecules toward them; this phenomenon is known as compression. Every solvent has a limit for compression and is known as limiting compressibility. The increase of adiabatic compressibility (β) with increase in temperature might be due to molecular interaction in solution which supports solvent–solute interactions as shown from fig 3.

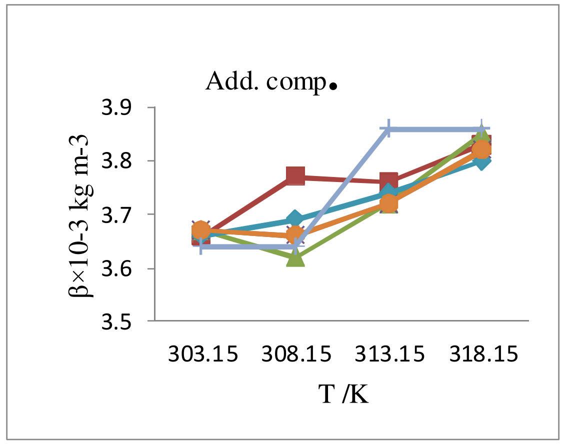
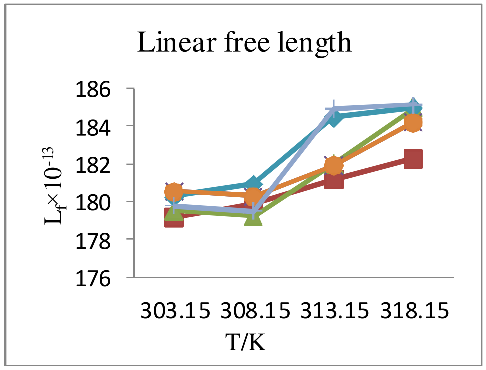


Figure 4.The temperature dependence of adiabatic compressibility of solutions of NNDMF+Water --■--, NNDMF+Water +L_1--▲-, NNDMF+Water +L_2--×--, NNDMF+Water +L_3--♦--, NNDMF+Water +L_4-●-- and NNDMF+Water +L_5 --+-in NNDMF+Water with concentration of 1×10^{-2}M.

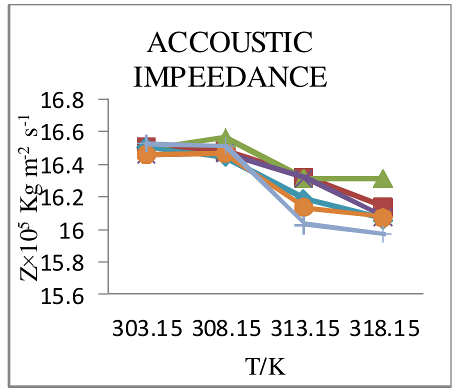
Table 3. Experimental values of, density, adiabatic compressibility, relative association, acoustic impedance, linear free length etc of L_1, L_2, L_3, $L_4$and L_5 in NNDMF at different temperatures with conc. 1×10^{-2}M

T/K	$\beta_s\times10^{-10}$, Nm^{-2}	R_A	$Z\times10^5$ kg^{-2}ms^{-1}	$\Phi_v\times10^{-4}$ cm^3 mol^{-1}	$L_f\times10^{-13}$
		L_1			
303.15	3.62	0.992	16.49522	-4539.37	179.57
308.15	3.67	1.005	16.56346	-6267.65	179.26
313.15	3.72	1.017	16.31012	-4963.25	182.01
318.15	3.85	1.005	16.31012	-7908.9	184.99
		L_2			
303.15	3.66	0.994	16.45888	-7263	180.55
308.15	3.69	1.007	16.46726	-5358.77	180.3
313.15	3.72	1.008	16.31347	-4558.17	181.93
318.15	3.82	1.003	16.07487	-3863.1	184.23
		L_3			
303.15	3.69	0.997	16.50513	-7868.3	180.31
308.15	3.73	1.008	16.44209	-859265	180.96
313.15	3.75	1.019	16.1872	-7191.9	184.5
318.15	3.8	1.017	16.06068	7929.9	184.99
		L_4			
303.15	3.66	0.994	16.45887	-7263	180.55
308.15	3.67	1.007	16.46726	-5358.77	180.3
313.15	3.72	1.0085	16.13465	-4558.17	181.93
318.15	3.82	1.003	16.07487	-3863.1	184.23
		L_5			
303.15	3.64	0.993	16.52696	-4337.59	179.81
308.15	3.68	1	16.51021	-3032.61	179.54
313.15	3.83	1.014	16.0299	-2329.68	184.95
318.15	3.86	1.002	15.96996	-2230	185.17

The variation of ultrasonic velocity in a solution depends on the intermolecular free length on mixing. On the basis of a model for sound propagation given by Erying and Kincaid[18], ultrasonic velocity increases with decrease of free length (L_f) and vice versa.



Intermolecular free length is a predominant factor for determining the variation of ultrasonic velocity, in liquids and their solutions[19]. Intermolecular free length is the distance between the surfaces of the neighboring molecules and indicates a significant interaction between solute–solvent as well as solvent–solvent molecules[8] denoted by fig 4. Hence, it is also a good tool to



investigate the molecular interactions in the binary solvent mixture.

Figure 5. Variation of linear free length (L_f) of NNDMF--■--, NNDMF+L_1--▲-, NNDMF+L_2--×--,, NNDMF+L_3--♦--, NNDMF+L_4-●-- and NNDMF+L_5 --+-in NNDMF with concentration of 1×10^{-2}M.

Figure 6. Variation of acoustic impedance of NNDMF--■--, NNDMF+L_1--▲-, NNDMF+L_2--×--,, NNDMF+L_3--♦--, NNDMF+L_4-●-and NNDMF+L_5--+- in NNDMF with concentration of 1×10^{-2}M.

When the ultrasonic wave travels through a solution, some part of it travels through the medium and remaining part of ultrasonic wave gets reflected by the solute [20] it means solutes restricts free flow of sound wave. The character that decreases this restriction or backward movement of sound waves is known as acoustic impedance (Z). If the temperature increases, ultrasonic velocity decreases and value of acoustic impedance (z) decreases[19] as acoustic impedance (Z) is the product of ultrasonic velocity (u) and density (ρ). The apparent molal volume behaves same way as that of the adiabatic compressibility in the solution, hence from fig 5 it is clear that as temperature increases acoustic impedance decreases which supports solute solvent interaction . The negative values of (ϕ_v) indicate electrostatic solvation of ions. To examine the solute-solvent interactions, ϕ_v values are negative and increase with a rise in temperature[21]. This indicates the presence of solute-solvent interactions, and these interactions are strengthened with a rise in temperature and vice versa. From the observation table 2 it is also seen that value of relative association (R_A) increases along with temperature. The value of R_A depends on breaking of bonds of solvents molecule due to the addition of solute and salvation of the solute.

CONCLUSIONS:

The ultrasonic method is powerful tool for characterizing physicochemical properties and existence of molecular interaction in the mixture. The result reveals that the density and ultrasonic velocity of pure NNDMF and ligand solutions decreases with increase in temperature. It is also seen that the formation of linear plot between and respective parameters indicated that the stronger solute-solvent interaction.

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