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Research Paper



Acoustical studies of some 1,3,4-thiadiazole derivatives in acetone at 303.15 k

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Abstract

Some new 1, 3, 4-thiadiazole have been synthesized and characterized by IR and NMR spectra. Densities, viscosities and ultrasonic velocities of these compounds have been measured over the wide composition range at 303.15 K in acetone. From these data, various acoustical parameters were evaluated. Some these parameters are adiabatic compressibility, intermolecular free length, relaxation strength, relative association, Rao's molar constant, salvation number etc. The behaviour of solutions of these compounds in acetone is explained from the evaluated parameters.

Keywords: *1, 3, 4-Thiadiazole, density, velocity, Acetone, acoustical properties.*

1. Introduction

The study of molecular interaction plays a vital role in the development of molecular science. Molecular interactions and structural behavior of molecular and their mixtures can be identified using ultrasonic studies. At present, ultrasonics is a subject of extensive research and we find its usefulness in the fields of biology, biochemistry, engineering, geography, geology, medicine, polymer industry etc. It has also been applied to process monitoring and materials characterization [1]. Ultrasonic velocity together with density and viscosity data furnishes a wealth of information about the interaction between ions, dipoles; hydrogen bonding, multipolar and dispersive forces [2] [6].

A literature survey reveals that ultrasonic velocity of various organic, inorganic and biological compounds in various solvents have been studied [7-9]. Many researchers have studied acoustical studies of some Schiff bases in various solvents and 1, 2, 4-triazole derivatives in DMF and THF [10] [14].

1, 3, 4-oxadiazole derivatives have attracted considerable attention because of their biological and electrochemical properties [15]. The wide spread use of 1, 3, 4-oxadiazoles as a scaffold in medicinal chemistry establishes this moiety as an important bioactive class of heterocycles. These molecules are also utilized as pharmacophores due to their favorable metabolic profile and ability to engage in hydrogen bonding. Therefore the applications of these compounds attract us to study their behaviour in acetone.

2. Experimental

The solvent used in the present work of AR grade and were purified according to the standard procedure described in the literature [16]. The Compounds were recrystalized before use. Solutions of different molarity were prepared for each binary system. The ultrasonic velocity in the mixture was measured using a variable path fixed frequency ultrasonic interferometer working at 2 MHz frequency (Mittal enterprises, New Delhi). The accuracy of sound velocity was ±0.1 ms-1.

The density was determined at the experimental temperature using 10ml capacity specific gravity bottle immersed in a thermostatic bath (accuracy +0.010C). The volume of the bottle at the experimental temperatures, viz. 303.15K was ascertained using doubly distilled water. The densities of water at these temperatures were obtained from literature. The viscosity of pure liquids and liquid mixtures at 303.15K were determined using an Ostwald viscometer.

3. Results and discussion

Various acoustical parameters like adiabatic compressibility (βad), intermolecular free length (Lf), specific acoustical impendence (Zi), Rao's molar sound function (R), Vander Waals constant (b), etc., were evaluated using the following standard equations [17], [29].

1) Adiabatic compressibility, $\beta_{ad} = 1/u^2\rho$

2) Intermolecular free length, $L_f = K/u\rho^{1/2}$

3) Relative association, $(R.A) = \left(\frac{\rho}{\rho_o}\right)\left(\frac{C_o}{C}\right)^{1/3}$

4) Specific Acoustic impedance, $z_i = P_e/C$

5) Viscous relaxation time, $\tau = \frac{4}{3}\beta\eta$

6) Relaxation strength, $r = 1 - \left(\frac{u}{u_\alpha}\right)^2$

7) Rao's constant or molar sound velocity, $R = Vu^{1/3}$

8) Wada's constant, $B' = \frac{M}{\rho}K_s^{1/7}$

9) Ultrasonic attenuation, $\frac{\alpha}{f^2} = \frac{8\pi^2\eta}{3u^3\rho}$

10) Vander Waal's constant,

$$b = \frac{M}{\rho}\left\{1 - \left(\frac{RT}{MC^2}\right)\left[1 + \left(\frac{MC^2}{RT}\right)^{1/2} - 1\right]\right\}$$

11) Isothermal compressibility, $\beta_T = \frac{1.71\times10^{-3}}{T^{4/9}u^{1/2}\rho^{1/3}}$

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12) Isothermal expansion co-efficient, $\alpha = (0.0191\beta_T)^{1/4}$

13) Internal pressure, $\pi_i = \frac{\alpha T}{\beta_T}$

14) Free volume, $V_f = \left(\frac{bRT}{\pi_i}\right)^3 \left(\frac{1}{V^2}\right)$

15) Solvation number, $S_n = \left(\frac{n_1}{n_2}\right)\left(1 - \frac{\beta}{\beta_0}\right)$

Where all the notations having the uaual meanings and the experimental data of u, ρ and η are given table 1. Table shows that, in each system velocity increases with concentration of 1, 3, 4-thiadiazole derivatives in acetone (shown in fig. 1). This indicates that solute-solvent interaction observed at higher concentrations of solute. Figure 2 and 3 shows the variation of density and viscosity with concentration for all systems.

Ultrasonic velocity depends on intermolecular free length inversely. The velocity increases with decreases in L_f. Free length (L_f) decreases continuously which suggest that there is strong interaction between solvent (acetone) and compound molecules. Free length, which is an intermolecular property defined as the distance between the surfaces of the molecules, are also evaluated from the values of adiabatic compressibilities. Evaluated L_f values are given in Table 2. The variations are shown in fig.4.

The adiabatic compressibility of the solutions in acetone is also found to decrease with increase of concentration (fig-5). This phenomenon can also be explained by assuming that the solvated molecules are fully compressed by the electrical forces of the ions. Due to solute-solvent concentrations in the system, compressibility of the solution decrease with the increase in solute concentration. This is further confirmed by decrease of L_f and relaxation strength (r) values. The association between solute-solvent molecules is further confirmed by relative association values, which are found to increase continuously with concentration for all the compounds in acetone.

The Rao's molar sound function, Van der Waal's constant and molar compressibility (W) for all the solutions are observed to increase linearly, which suggest that a weak solute-solvent interaction takes place.

The internal pressure is the resultant of forces of attraction and repulsion between the molecules in a solution. Table 3 shows that the internal pressure increases with increasing concentration of solute, which indicates the primary effect of dissolving solute lowers the compressibility of the solvent molecules. The lowering of compressibility results in the increase of ultrasonic velocity and hence π_i increases with the concentration of solute (in fig 10). S.Ravichandran et al., [30] is explained the similar trend in aqueous zinc nitrate system. π_i also gives an idea of the solubility characteristics. Dissolved solutes exist under the π_i of the medium and their interactions with solvent arise may be due to hydrogen bonding [31].

This is further supported by free volume. The free volume of a solute molecule at a particular temperature and pressure depends on the internal pressure of a liquid, in which it is dissolved. Thus, free volume is an inverse function of internal pressure. From table 3 that a decrease in free volume and increase in π_i with increase in concentration of solute respectively, which attributed to the increase in magnitude of interaction.

Similar trend is elucidated in aniline and is bound to combine with the other components [32]. Vasantharani et al., [33] is also revealed the decrease in V_f shows that the clustering is due to dipole-induce dipole interaction. It is primarily due to the formation of spherical cage-like structure owing to the closer packing of the molecule. Figure 11 shows the regular fall in V_f with the molefraction of solute may be attributed to the close approach of the molecules [34], [35].

The interactions occurring in different solutions can also be confirmed by the solvation number (Sn), which is measure of structure forming or structure breaking tendency of solute in a solution. Fig. 12 shows the variation of solvation number (Sn) with molefractions for all the compounds in acetone. Sn values are found decrease with concentration of solute in acetone (shown in table 3). The decrease in solvation number suggests increase in structure breaking tendency of compound in a solution. This suggests that structure breaking tendency decreases with concentration in most of the compounds, which may be due to weak dipole-induced dipole interactions or steric hindrance. Such interactions may cause weakening between solute and solvent molecules. Sn clearly represents the solvation of solute in solvent causes interactions giving rise to increase the solubility of solute [36].

This weak association is further confirmed by low relative association value (RA), this is almost same for all compounds (Table 3). The decrease of relative association with concentration substantiate that the solvent structure breaks up.

Further, as these systems are characterized by hydrogen bonding, the solute-solvent interactions can be interpreted in terms of structural changes that arise due to hydrogen-bond interactions between various components.

4. Conclusion

Ultrasonic method is a powerful probe for characterizing the physico-chemical properties and existence of molecular interaction in the mixture. In addition, density, viscosity, velocity and the derived parameters provide evidence of confirmation.

In the present investigation, density, viscosity and ultrasonic velocity have been measured in non-aqueous solution of synthesized 1, 3, 4-oxa and thiadiazole derivatives at 303.15K. With increase in concentration of solution, the experimental density, ultrasonic velocity, viscosity and computed Acoustic impedance (Zi), Rao's constant (R), Wada's constant (W) and internal pressure values increase, while compressibility (βad), intermolecular free length (Lf), relaxation strength (r), free volume decrease. These suggest predominance of solute-solvent interactions. A novel bindings' are introduced between the solute and the solvent molecules. Thus a decrease in the free solvent molecules leads to decrease the value of RA and βad

Further, as these systems are characterized by hydrogen bonding, the solute-solvent interactions can be interpreted in terms of structural a change that arises due hydrogen bond interactions between various components of the solvent solution systems. Acetone belong to the carbonyl series having functional group of C=O, While thiadiazole derivatives belong to nitrile series having functional group C-NH2 and aromatic rings.

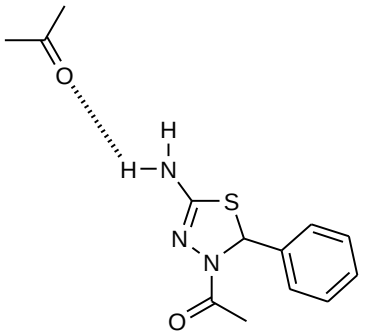


Table 1: Velocity (u), Density (ρ), Viscosity (η) and Molar volume (Vm) of 2, 5-disubstituted-1, 3, 4-thiadiazole derivatives with Acetone at 303.15K.

Mole fraction	1,3,4-Thiadiazole derivatives			
X_2	u ms^{-1}	ρ kgm^{-3}	η × 10^3 $Nm^{-1}sec$	Vm ×10^6 m^3/mol
		Compound AT1		
0.0063	1202.93	795.75	0.60	74.28
0.0125	1212.67	796.26	0.67	75.51
0.0250	1291.53	800.19	0.70	77.69
0.0500	1360.07	800.45	0.76	82.76
0.1000	1429.67	806.42	0.82	92.27
		Compound AT2		
0.0063	1224.13	784.06	0.53	75.93
0.0125	1274.13	785.84	0.57	77.59
0.0250	1290.07	788.00	0.62	81.05
0.0500	1363.00	791.17	0.66	88.03
0.1000	1436.80	798.41	0.73	101.71
		Compound AT3		
0.0063	1269.67	783.30	0.50	75.94
0.0125	1292.93	785.58	0.54	77.49
0.0250	1360.07	786.35	0.59	80.97
0.0500	1420.27	791.05	0.64	87.54
0.1000	1438.87	798.41	0.70	100.71

Table 2: Adiabatic compressibility (βad), intermolecular free length (Lf), Specific acoustic impedance (Zi), Rao's constant (R), Wada's constant (W), Vander waal's constant (b) and Ultrasonic attenuation (α/f²) of 2, 5-Disubstituted-1, 3, 4-Thiadiazole derivatives with Acetone at 303.15K.

Mole fraction X_2	βad ×10^9 Pa^{-1}	L_f ×10^{10} m	Z_i ×10^6 $kgm^{-2}s$	R ×10^6 $m^{10/3}/kgs^{1/3}mol$	W ×10^{-3} $(m^3/kg.mol)(kg/ms^2)^{-1/7}$	b ×10^3 m^3/mol	α/f² ×10^{14} sec
				Compound AT1			
0.0063	0.8684	0.6178	0.96	789.97	1.46	68.79	1.1446
0.0125	0.8540	0.6126	0.97	805.25	1.49	70.00	1.2443
0.0250	0.7420	0.5738	1.03	846.06	1.56	72.33	1.0646
0.0500	0.6754	0.5448	1.09	916.96	1.69	77.40	0.9870
0.1000	0.6067	0.5164	1.15	1039.43	1.91	86.77	0.9138
				Compound AT2			
0.0063	0.8511	0.6116	0.96	812.23	1.50	70.40	0.9744
0.0125	0.7839	0.5870	1.00	841.21	1.55	72.15	0.9268
0.0250	0.7625	0.5790	1.02	882.31	1.63	75.51	0.9635
0.0500	0.6836	0.5468	1.08	976.02	1.80	82.45	0.8623
0.1000	0.6067	0.5164	1.15	1147.70	2.11	95.88	0.8060
				Compound AT3			
0.0063	0.7919	0.5900	0.99	822.29	1.53	70.55	0.8265
0.0125	0.7648	0.5785	1.02	844.22	1.56	72.11	0.8362
0.0250	0.6875	0.5497	1.07	897.07	1.65	75.65	0.7775
0.0500	0.6267	0.5248	1.12	984.02	1.81	82.15	0.7425
0.1000	0.6050	0.5157	1.15	1137.01	2.09	94.92	0.7705

Table 3: Relaxation strength (r),Viscous relaxation time (τ), Isothermal compressibility (βτ), Isothermal expansion co-efficient (α), Internal pressure (πi) and Free volume (Vf), Solvation number (Sn) and Relative Association (RA) of 2,5-Disubstituted-1,3,4-Thiadiazole derivatives with Acetone at 303.15K

Mole fraction X_2	r	τ ×10^{12} Sec	βτ × 10^{14} m^2N^{-1}	α ×10^{-4} K^{-1}	π_i ×10^{-12} m^2N^{-1}	V_f×10^{19} m^3mol^{-1}	S_n ×10^{-2}	R.A
				Compound AT1				
0.0063	0.4347	0.6982	1.2643	1.2466	2.9890	8.6935	2.2912	0.8617
0.0125	0.4256	0.7652	1.2430	1.2413	3.0273	8.0965	1.2612	0.8600
0.0250	0.3484	0.6973	1.0887	1.2008	3.3438	5.6761	1.0503	0.8462
0.0500	0.2774	0.6808	0.9813	1.1701	3.6146	3.9595	0.6794	0.8321
0.1000	0.2016	0.6625	0.8793	1.1384	3.9247	2.4888	0.4052	0.8244
				Compound AT2				
0.0063	0.4147	0.6049	1.2452	1.2419	3.0233	8.0400	2.5685	0.8441
0.0125	0.3659	0.5989	1.1460	1.2163	3.2177	6.3856	1.8230	0.8348
0.0250	0.3499	0.6304	1.1137	1.2077	3.2873	5.4890	0.9970	0.8337
0.0500	0.2743	0.5960	0.9924	1.1734	3.5843	3.5894	0.6630	0.8218
0.1000	0.1936	0.5873	0.8823	1.1394	3.9148	2.0637	0.4052	0.8149
				Compound AT3				
0.0063	0.3703	0.5322	1.1590	1.2198	3.1904	6.8394	3.5166	0.8331
0.0125	0.3470	0.5483	1.1134	1.2076	3.2881	5.9998	2.0022	0.8305
0.0250	0.2774	0.5362	1.0048	1.1770	3.5509	4.3636	1.2979	0.8174
0.0500	0.2120	0.5348	0.9142	1.1495	3.8119	3.0174	0.7704	0.8105
0.1000	0.1913	0.5622	0.8797	1.1385	3.9233	2.0911	0.4070	0.8145

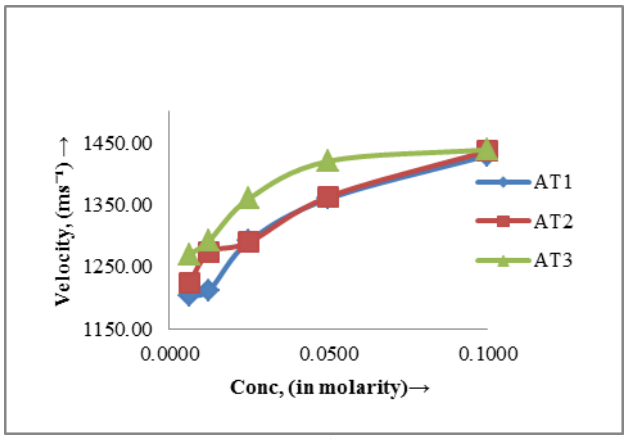


Fig. 1: Velocity Vs Concentration of AT1, AT2 and AT3 at 303.15K

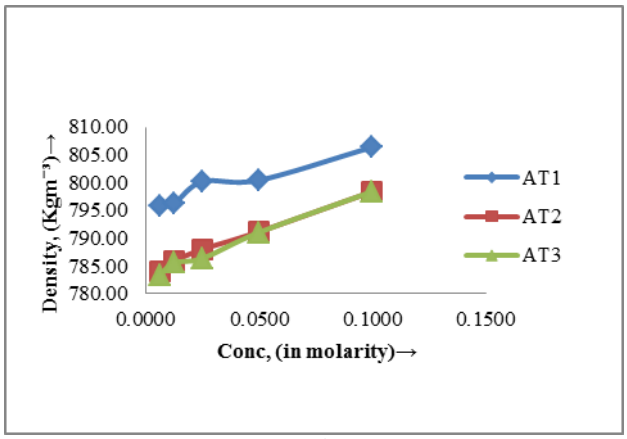


Fig. 2: DensityVs Concentration of AT1, AT2 and AT3 at 303.15K

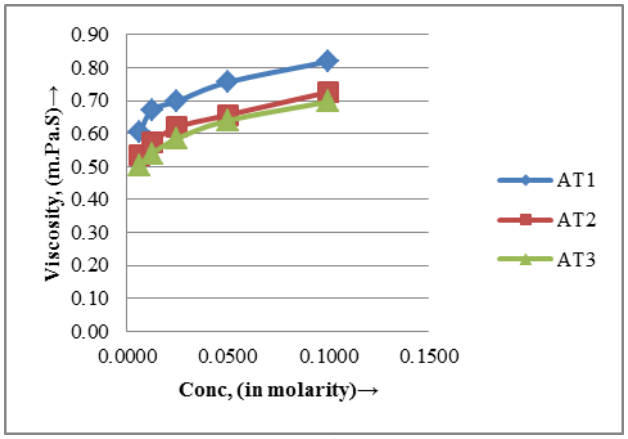


Fig. 3: Viscosity Vs Concentration of AT1, AT2 and AT3 at 303.15K

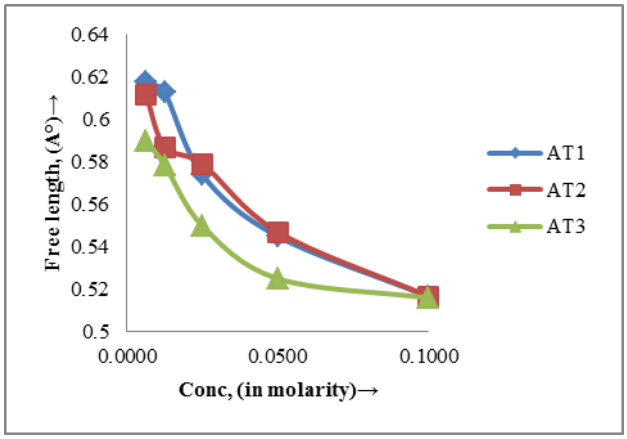


Fig. 4: Free length Vs Concentration of AT1, AT2 and AT3 at 303.15K

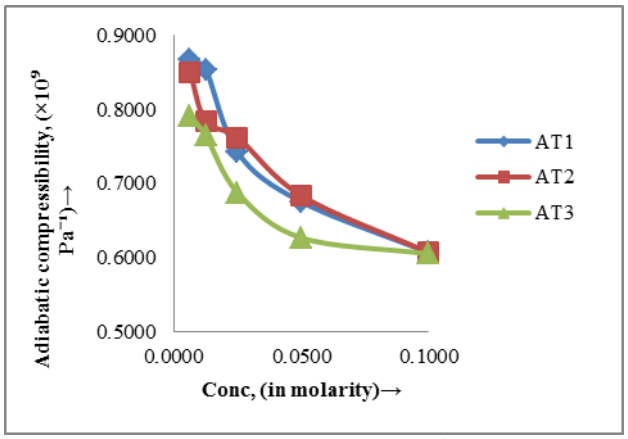


Fig. 5: Adiabatic compressibility Vs Concentration of AT1, AT2 and AT3 at 303.15K

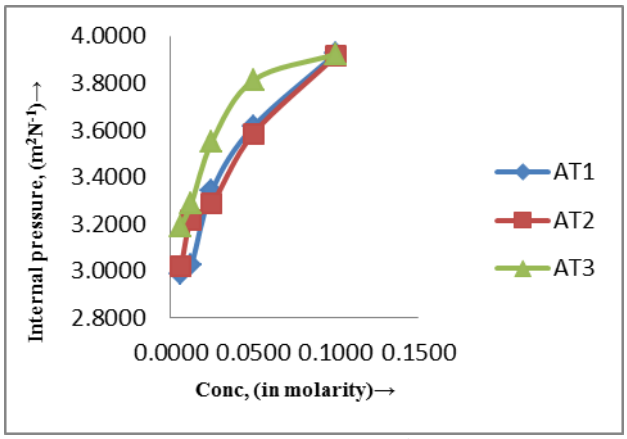


Fig. 6: Internal pressure Vs Concentration of AT1, AT2 and AT3 at 303.15K

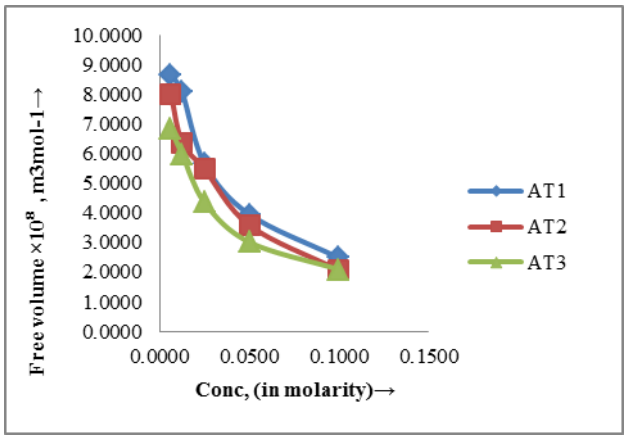


Fig. 7: Free volume Vs Concentration of AT1, AT2 and AT3 at 303.15K

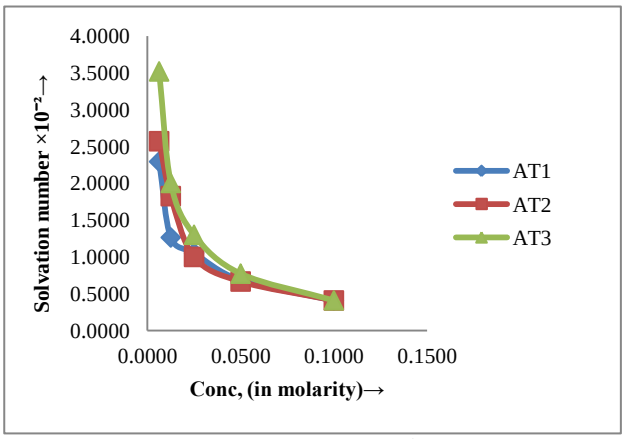


Fig. 8: Solvation number Vs Concentration of AT1, AT2 and AT3 at 303.15K

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