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Acoustical investigation of binary mixtures of 8,10-dinitro-7h-benzo[c]carbazole in Ethanol, Acetone, DMF at different concentrations , 308.15 K

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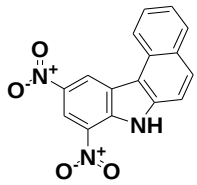
Abstract-Ultrasonic velocity, density and viscosity of binary mixture 8,10-dinitro-7H-benzo[c]carbazole-70% Ethanol, 8,10-dinitro-7H benzo[c]carbazole – 70% Acetone, and 8,10-dinitro-7H-benzo[c]carbazole – 70 % DMF were measured at different concentrations of 8,10-dinitro-7H-benzo[c]carbazole and temperature at 308.15 K. Acoustical parameter like Acoustic impedance, Adiabatic compressibility, Relaxation time, Linear free length, Relative association, Lenard Jones Potential, Rao's constant, and Sound velocity number were determined from experimental data of density, viscosity and ultrasonic velocity. The effect of concentration variations in the strength of molecular interaction has been studied. Effective correlation was observed in terms of solute–solvent and solvent–solvent interaction at all concentrations.

Keyword-Ultrasonic velocity, density, viscosity, acoustical parameter, 8,10-dinitro-7H-benzo[c]carbazole.

1. INTRODUCTION

Carbazole and its derivatives are an important type of nitrogen containing aromatic heterocyclic compounds, possess desirable electronic and charge transport properties, as well as large π- conjugated system, and the various functional groups are easily introduced into the structurally rigid carbazole ring[1]. Carbazole ring is present in a variety of naturally occurring medicinally active substances. For example, the Carbazomycin are an unprecedented class of antibiotics with a carbazole framework[2-3]. These characteristics result in the extensive potential applications of carbazole-based derivatives in the field of medicinal chemistry (antitumor, antimicrobial, antihistaminic, antioxidative, anti-inflammatory, psychotropic agents.)[4].



Structure of 8,10-dinitro-7*H*-benzo[*c*]carbazole

The studies of solution properties of liquid solution of polar and non-polar components have great applications in industrial and technological process[5].The recent publications in this area shows that the many researchers give attention toward study of ultrasonic velocity measurement and study of acoustical properties.[6]

In view of broad biological activity of carbazole, due to this we here plan to study possible theoretical approach for the determination of ultrasonic parameters are useful for the studies of physicochemical properties and molecular interaction of any binary liquid.

2. MATERIAL AND EXPERIMENTAL

The solvent Ethanol, Acetone, DMF (sigma-Aldrich) of analytical grade used without purification. The compound 8, 10-dinitro-7H-benzo[c] carbazole synthesize by known method.[7,8] The liquid mixture of different composition were prepared by calculated volume of each component .The densities of Ethanol, Acetone, DMF and 8,10-dinitro-7H-benzo[c] carbazole solution were measured by using specific gravity bottle , mass measurements electronic balance and the viscosity was measured using Ostwald's viscometer. The ultrasonic velocities of pure components and their mixture were measured by ultrasonic interferometer (Mittal enterprises, model F-81s) at 2 MHz having accuracy ± 1 ms^{-1} in velocity.

3. THEORY

Ultrasonic velocity can be used to calculated thermodynamic and acoustic parameter, which more reliable, precise and very useful in the study of molecular interaction in binary liquid mixture. Given acoustical parameters are calculated by using various equations.

Ultrasonic velocity (U):

The ultrasonic can be measured using ultrasonic interferometer at the frequency 2MHz [9.]

$$U = v\lambda \quad (1)$$

Where, U is the ultrasonic velocity, λ is the wavelength.

Acoustic Impedance (Z):

Acoustic impedance is found to be almost inversely to the adiabatic compressibility. The relation is given by [10]

$$Z = u\,\rho \qquad (2)$$

Where, p is the density and u is the ultrasonic velocity

Isentropic Compressibility (βs):

Adiabatic compressibility can be calculated from the speed of sound (u), and the density of the medium (ρ).The relation is given by [11].

$$\beta s = 1/\rho u^2 \qquad (3)$$

Where, ρ is density, u is speed of sound.

Relaxation time (τ):

The relaxation time calculated from the adiabatic compressibility (β) and viscosity (η) using the relation is given by [12].

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

Intermolecular Free Length (Lf):

The adiabatic compressibility of a liquid can be expressed in terms of the intermolecular free length which is the distance between the surfaces of the neighboring molecules and is given by[13].

$$L_f = K\,\beta s^{1/2} \qquad (5)$$

Where, K is Jacobson constant.

Relative Association (R_A):

The relative association has been determined using the standard formula[14].

$$R_A = (\rho/\rho_o)\,(u_o/u)^{1/3} \qquad (6)$$

Where, ρ_o ρ are the densities and u_0 u are the ultrasonic velocities of the solvent and the solution.

Sound Velocity Number (U):

Sound velocity number is calculated from following equation-

$$U = u\text{-}u_o/u_o c \qquad (7)$$

U is the sound velocity number; c is the concentration of the solute.

Rao's Constant (R):

Rao's noted that the ratio of temperature coefficient of sound velocity u to the expansion coefficient V is virtually same for all but it is not associated with organic liquid. According to the Rao's

$$R = u^{1/3} V \qquad (8)$$

Lenard-Jones Potential (LJP):

$$LJP = 6Vm/Va \qquad (9)$$

Where, Vm represent the molar volume and Va represent the available volume.

4. RESULTS AND DISCUSSION

Experimental determined values of ultrasonic velocity u (ms^{-1}), density ρ (g cm^{-3}) and viscosity η (10^{-3} Nsm^{-2}) for the binary mixture of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol , 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone and 8,10-dinitro-7H-benzo[c] carbazole DMF solutions at temperatures 308.15 K are given in **Table 1**.

From fig 1 it is observed that ultrasonic velocity increases with increase in concentration of 7-hydroxy-4-phenyl-2H-chromen-2-one at constant temperature, also fig 2 and 3 indicates increase of density and viscosity with increase in concentration of solute at constant temperature. An increase in concentration allows for a closer approach of solvent and solute molecules, and stronger association between solute and solvent molecules. This leads to decrease in the volume and an increase in the density of the solution [15]. The increase values of viscosity and ultrasonic velocity indicates molecular association in the experimental systems, which is possible due to the presence of amine group solute structure, it is notable that molecular interactions are less at lower values of velocities [16]. It may be due to breaking of molecular clusters, presence of dipole-dipole interaction, solute – solvent interactions, solvent - solvent interactions and presence of hydrogen bonding between solute molecule and water molecule solvents.

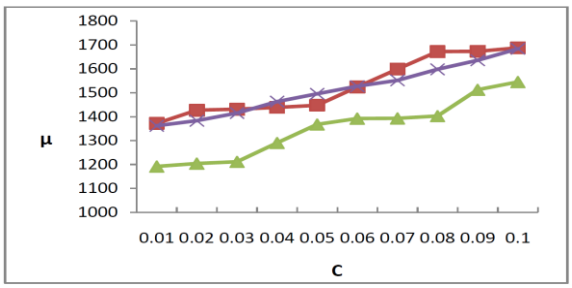


Figure 1 Ultrasonic velocity (u) plotted against concentration of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol (■) , 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c] carbazole DMF (×) binary mixture at 307.15 K.

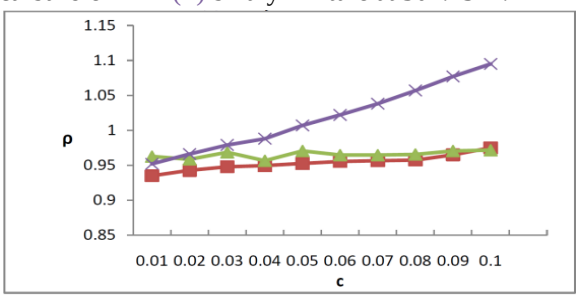


Figure 2 Density (ρ) plotted against concentration of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol (■), 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c]carbazole DMF (×) binary mixture at 307.15 K.

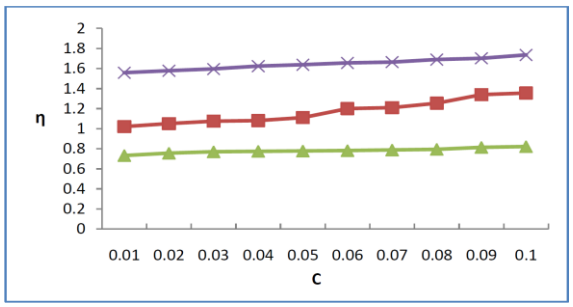


Figure 3 viscosity (η) plotted against concentration of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol (■), 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c]carbazole DMF (×) binary mixture at 307.15 K.

Table 1. Experimental values of ultrasonic velocity, density and viscosity of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol (■), 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c]carbazole – 70% DMF (×) binary mixture at 307.15 K. [8,10-dinitro-7H-benzo[c]carbazole - L]

C,mol/lit	u, m s^{-1}			(ρ) kg m^{-3}			(η) × 10-3 Nsm^{-2}		
	70% Ethanol+L	70% Aceton+L	70% DMF+L	70% Ethanol+L	70% Acetone+L	70% DMF+L	70% Ethanol+L	70% Acetone+L	70% DMF+L
0.01	1372	1192	1362	0.9322	0.9626	0.952	1.021	0.733	1.558
0.02	1427	1204	1383	0.9427	0.9586	0.966	1.051	0.756	1.578
0.03	1431	1212	1415	0.9478	0.9686	0.979	1.075	0.77	1.595
0.04	1439	1291	1463	0.9496	0.9566	0.988	1.081	0.775	1.624
0.05	1448	1368	1496	0.9525	0.9706	1.007	1.111	0.778	1.638
0.06	1524	1392	1527	0.9555	0.9646	1.022	1.2	0.782	1.656
0.07	1599	1393	1552	0.9566	0.9646	1.038	1.21	0.788	1.664
0.08	1672	1403	1598	0.9575	0.9656	1.057	1.255	0.795	1.689
0.09	1673	1513	1636	0.965	0.9706	1.077	1.34	0.814	1.702
0.1	1688	1545	1684	0.975	0.9716	1.095	1.356	0.822	1.735

When the ultrasonic wave propagate through a solution, some part of it move through the medium and remaining part of ultrasonic wave gets reflected by the solute [17],it indicate that solutes will restrict free flow of ultrasonic wave. The property that decreases this shortening or astern movement of ultrasonic waves is known as acoustic impedance (Z). The specific acoustic impedance is dependent on both concentration and temperature of the solution. As the internal pressure and cohesive energy [18] increases with solute concentration, strong dipole-dipole and solute-solvent interaction occurs between 8,10-dinitro-7H-benzo[c] carbazole which is solute Ethanol , Acetone and DMF which are solvents which is evident from fig 4. Hence, an increase in specific acoustic impedance is due to rise in instantaneous pressure occurs on any molecule in the given experimental system with traveling of a sound wave. The linear variation in acoustic impedance with concentration confirms the presence of molecular association between the solute–solvent molecules, also increasing trends of impedance further support the possibility of molecular interaction between the solute–solvent [19].

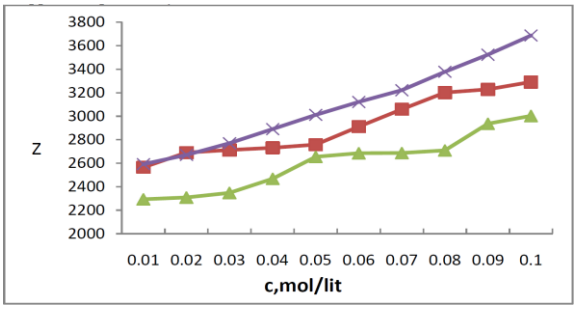


Figure 4 Acoustic impedance (Z) plotted against concentration of 8,10-dinitro-7H-benzo[c] carbazole -70% Ethanol,8,10 dinitro-7H-benzo[c]carbazole–70% Acetone and 8, 10-dinitro-7H-benzo[c] carbazole–DMF, at 307.15 K.

From fig 5, it is found that adiabatic compressibility (βs) decreases with increase in concentration of solution it is due to the fact that surrounded molecules experience electrostatic field [20] due ions. These decrease values of compressibility indicate that there is an increase in molecular association with increase in solute concentration, as new species form due to the molecular association become compact and less compressible. These also suggest that compressibility of solvent is greater than that of solution. The increase in adiabatic compressibility also indicates a change in the conformation/orientation of the solute molecules in solution, leading to weaker inter-molecular interaction. This is attributed to the steric requirement of arranging an increasing number of large molecules.

In this situation, the steric factor takes predominance over intermolecular interactions. An increase in isentropic compressibility indicates a change in the orientation of the solvent molecules around the 8,10-dinitro-7H-benzo[c] carbazole (solute) molecule undergoing conformational change, which results in weakening of the solute-solvent interactions. The formation of weaker intermolecular interaction leads to an increase in adiabatic compressibility. It also indicates the associating tendency of the solute molecules in solution.

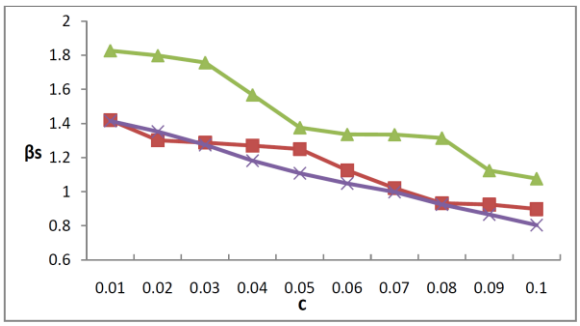


Figure 5 Adiabatic compressibility (βs) plotted against concentration of 8,10-dinitro-7H-benzo[c] carbazole -70% Ethanol (■), 8, 10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c] carbazole DMF (×) at 307.15 K

Relaxation time (τ) is the time taken for the excitation energy to appear as translational energy and it depends on temperature and impurities[21]. In the present case, relaxation time increases with increase in concentration of 8, 10-dinitro-7H-benzo[c] carbazole and decreases at high temperature (fig-6). The former indicates the presence of molecular interaction in the mixture, whereas the latter shows the instantaneous conversion of excitation energy to translational energy.

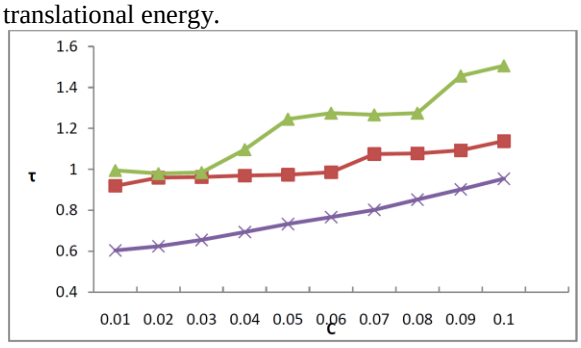


Figure 6 Relaxation time (τ) plotted against concentration of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol (■) , 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c] carbazole DMF (×) binary mixture at 307.15 K.

Intermolecular free length (L_f) is the distance between the surfaces of the neighboring molecules and indicates a significant interaction between solute–solvent as well as dipole-dipole interaction [22] in 8,10-dinitro-7H-benzo[c] carbazole-70% Ethanol , 8,10-dinitro-7H-benzo[c] carbazole -70% Acetone and 8, 10-dinitro-7H-benzo[c] carbazole-70% DMF solutions[23]. The decreasing value of intermolecular free length (L_f) indicates closer packing [24] which is evident from fig 7. The intermolecular free length on mixing of solute to the solvent is responsible for the variation of ultrasonic velocity of the same solution. On the basis of a model for sound propagation given by Erying and Kincaid [25] free length decreases with increases of ultrasonic velocity. Variation in free length indicates variation in the molecular forces in the mixture, which depends on the experimental density as well as the temperature of the mixture.

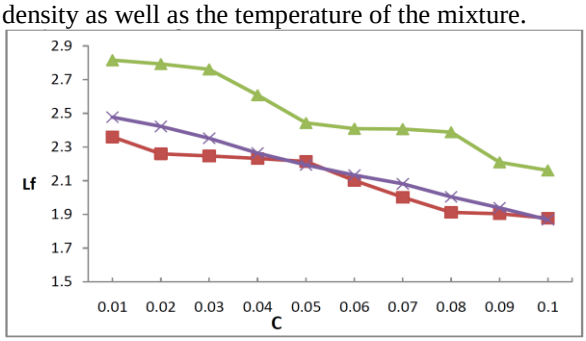


Figure 7 Linear free length (L_f) plotted against concentration of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol (■) , 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c] carbazole DMF (×) at 307.15 K

Increase in relative association with increase in of concentration of 8, 10-dinitro-7H-benzo[c] carbazole indicates presence of solute-solvent interaction, solvent-solvent interaction and hydrogen bonding which is evident from fig 8. It depends on either the breaking up of the solvent molecules on addition of solute molecules in solvent at certain temperature or the solvation of ions that are present [26].

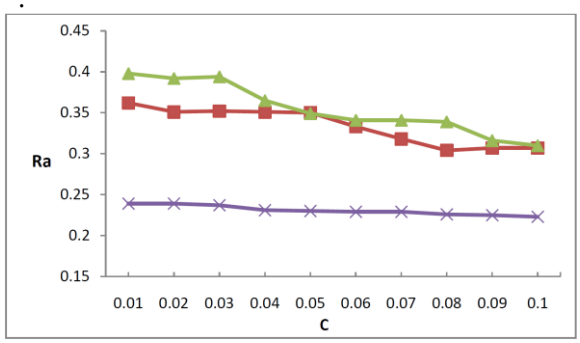


Figure 8 Relative association (R_a) plotted against concentration of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol (■) , 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c] carbazole DMF (×) at 307.15 K.

In general sound velocity number increases with increase in concentration of solute [27] and increase in temperature, however in present investigation same trend is observed with respect to the concentration of solute (fig 9).

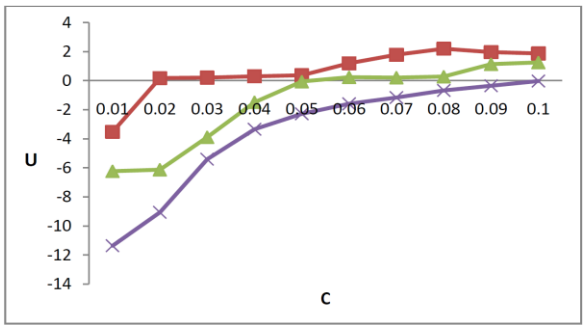


Figure 9 Sound velocity number (U) plotted against concentration of 8,10-dinitro-7H-benzo[c]carbazole - 70% Ethanol (■) , 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c] carbazole DMF (×) at 307.15K.

The plots of Rao's constant increases with increases in concentration for the binary mixture shows in fig 10, It clear that Rao's constant, is linear with concentration, shows weak induced dipole – induced dipole interaction in all binary system.

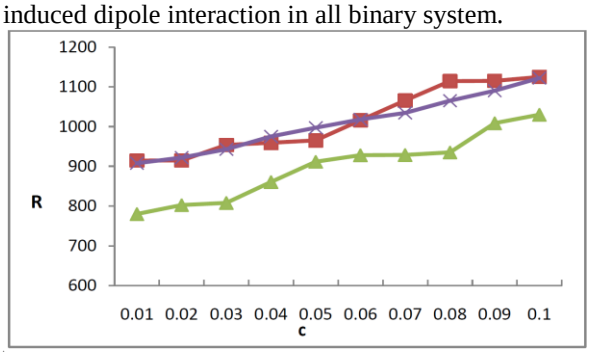


Figure 10 Rao's constant (R) plotted against concentration of 8,10-dinitro-7H-benzo[c]carbazole - 70% Ethanol (■) , 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8, 10-dinitro-7H-benzo[c] carbazole DMF (×) at 307.15 K.

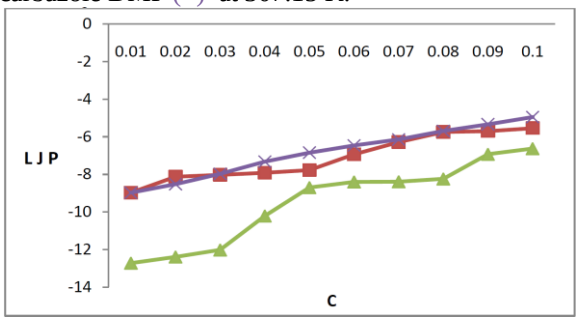


Figure 11 : Lenard Jones Potential (LJP) plotted against concentration of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol (■) , 8,10-dinitro-7H-benzo[c]carbazole – 70% Acetone (▲) and 8,10-dinitro-7H-benzo[c]carbazole DMF (×) at 307.15 K

The potential equation (LJP) accounts for the difference between attractive forces(Dipole-dipole, induced dipole, and London inter action) and repulsive forces ,the Values are calculated and shows in fig (11) ,the LJP value increases with increase in concentration of 8,10-dinitro-7H-benzo[c] carbazole fig (11). Indicates the presence of molecular interaction in the mixture indicate that dipole- dipole attraction are stronger than induced dipole – induced dipole interaction.

Table 2 : Acoustic impedance(z), Adiabatic compressibility(βs) ,Relaxation time(τ), Linear free length(L_f), Relative association(R_a), Rao's constant(R), Lenard Jones Potential(LJP), Sound velocity number(U) of 8,10-dinitro-7H-benzo[c]carbazole -70% Ethanol ,8,10 dinitro-7H-benzo[c]carbazole–70% Acetone and 8,10-dinitro-7H-benzo[c]carbazole–DMF solutions of different concentration at temperatures 308.15 K.

Sr.No.	C,mol/lit	$Z\times10^{-3}$ kg. m^2 s^{-1}	$\beta s\times10^{-10}$, m^2 N^{-1}	τ x 10^{-12} s	Lf (A^0)	Ra	R	L J P	U(kg mol^{-1})
70% Ethanol-8,10-dinitro-7H-benzo [c]carbazole									
1	0.01	2565	1.424	0.919	2.3662	0.361	914.66	-9.97	-3.516
2	0.02	2690	1.302	0.959	2.259	0.351	915.33	-8.12	0.175
3	0.03	2712	1.288	0.962	2.247	0.352	954	-8.02	0.21
4	0.04	2732	1.271	0.97	2.232	0.351	959.33	-7.91	0.298
5	0.05	2758	1.251	0.974	2.214	0.35	965.33	-7.77	0.365
6	0.06	2912	1.126	0.986	2.101	0.333	1016	-6.93	1.195
7	0.07	3059	1.022	1.075	2.001	0.318	1066	-6.28	1.778
8	0.08	3201	0.933	1.078	1.912	0.304	1114.6	-5.74	2.197
9	0.09	3228	0.925	1.093	1.904	0.307	1115.3	-5.69	1.961
10	0.1	3291	0.899	1.138	1.877	0.307	1125.3	-5.54	1.87
70% Acetone -8,10-dinitro-7H-benzo[c]carbazole									
1	0.01	2294	1.827	0.995	2.815	0.398	780	-12.72	-6.229
2	0.02	2308	1.799	0.98	2.793	0.392	802.6	-12.39	-6.122
3	0.03	2347	1.757	0.985	2.761	0.394	808	-12.02	-3.887
4	0.04	2469	1.568	1.097	2.608	0.365	860.6	-10.21	-1.475
5	0.05	2655	1.376	1.245	2.443	0.349	912	-8.7	-0.058

6	0.06	2685	1.337	1.275	2.408	0.341	928	-8.4	0.242
7	0.07	2687	1.335	1.267	2.406	0.341	928.6	-8.39	0.218
8	0.08	2709	1.315	1.275	2.388	0.339	935.3	-8.24	0.282
9	0.09	2937	1.125	1.456	2.209	0.316	1008.6	-6.93	1.141
10	0.1	3002	1.077	1.506	2.161	0.31	1030	-6.63	1.26
70% DMF -8,10-dinitro-7H-benzo[c]carbazole									
1	0.01	2593	1.415	0.604	2.477	0.239	908	-8.97	-11.36
2	0.02	2671	1.353	0.624	2.422	0.239	922	-8.52	-9.058
3	0.03	2770	1.275	0.655	2.352	0.237	943.3	-7.97	-5.407
4	0.04	2890	1.182	0.694	2.264	0.231	975.3	-7.32	-3.345
5	0.05	3012	1.109	0.733	2.193	0.23	997.3	-6.84	-2.285
6	0.06	3121	1.049	0.767	2.133	0.229	1018	-6.46	-1.598
7	0.07	3221	0.999	0.802	2.081	0.229	1034.6	-6.14	-1.158
8	0.08	3378	0.926	0.852	2.004	0.226	1065.3	-5.69	-0.673
9	0.09	3523	0.867	0.902	1.939	0.225	1090.6	-5.33	-0.348
10	0.1	3687	0.805	0.954	1.868	0.223	1122.6	-4.95	-0.029

Uncertainties in Z (velocity 1×10^{-3}),βs (0.01×10^{-10}, m^2N^{-1}),t (0.10×10^{-12}),L_f ($0.001A^0$), R_a(0.010, kg m^2), and U(0.1×10^{-5}, kg m^2) .

5. CONCLUSION

The nature of intermolecular interaction in a binary mixture solution has been explained on the basis of density, viscosity, ultrasonic velocity and acoustical parameter. result revels that density, viscosity, ultrasonic velocity aqueous solution increases with increases in concentration at 307.15K.From these measured physical property data, Acoustic impedance, Adiabatic compressibility, Relaxation time, Linear free length, Relative association, Rao's constant, Lenard Jones Potential, Sound velocity number are calculated. From above investigation it is found that 8, 10-dinitro-7H-benzo[c] carbazole shows interesting interactive behavior with solvent like ethanol, acetone and DMF.

The results also give the scope for investigation acoustical parameters of various substituted carbazole which help to used more applications of biological active carbazole.

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