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Ultrasonic Study of Molecular Interactions in Organic Liquids at Various Temperatures and Concentrations

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ABSTRACT

The ultrasonic velocity was measured for water and glacial acetic acid in their pure state and in their binary mixtures. The ultrasonic velocity was measured also for the solution of salicylic acid in glacial acetic acid. Relative density and relative viscosity were also measured at various temperatures and concentrations. The parameters like adiabatic compressibility, acoustic impedance, relaxation time and attenuation were determined. This study is helpful for the understanding of the macroscopic structure solute–solute and solute–solvent interactions.

Keywords*: Relative viscosity, acetic acid, ultrasonic velocity, molecular interaction*

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1. INTRODUCTION

The Ultrasonic technique is one of the good techniques for the study of intermolecular interactions in organic liquids [1–7]. The purpose of this paper is to use the ultrasonic interferometry for the measurement of ultrasonic velocity in acetic acid solution. The systems chosen here were acetic acid, water, their binary mixtures and solution of salicylic acid in acetic acid. The measurements were done at different concentrations and temperatures. The ultrasonic velocities were measured by ultrasonic interferometer, the relative density by pycnometer and the relative viscosity by Ostwald's viscometer. The measurements at different temperatures were conducted using constant temperature water bath. Concentration of acetic acid in water was in the range 0–3 N. The various parameters like adiabatic compressibility (β), acoustic impedance (Z), relaxation time (τ) and attenuation ($\frac{\alpha}{\pi^2}$) were computed by using the relations:

$$\beta = 1/ C^2\rho$$

$$Z = C\rho$$

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

$$\frac{\alpha}{\pi^2}=\frac{8\pi^2\eta}{3\rho C^3}$$

where, C is the ultrasonic velocity; ρ is the relative density in Kg/m^3, and η is the viscosity.

2. EXPERIMENTAL DETAILS

The liquids used were of analytic grade. The mixtures were prepared immediately before use by mixing appropriate volume. An electronic balance (Infra High Precision balance) with a precision of ±0.0001 g was used for mass measurements. The viscosity of the pure liquids and the liquid mixtures was measured by Ostwald viscometer at different concentrations and different temperatures. The viscometer was calibrated using distilled water. Constant temperature was maintained by using a Water bath (Equitron Stirred Waterbath with external pumping) with control accuracy ± 0.2ºC. The density of the liquids was measured by Pycnometer with an accuracy of ±5%. The Ultrasonic velocity of the liquids was measured by Ultrasonic interferometer (Mittal Enterprises, New Delhi) at frequency 2 MHz [8] with a tolerance of ±0.005%.

3. RESULTS AND DISCUSSION

The experimental results of ultrasonic velocity, density and viscosity of glacial acetic acid and the calculated values of adiabatic compressibility, acoustic impedance, relaxation time and attenuation at different temperatures are given in Table I. Comparing Tables I and II, it can be observed that the adiabatic compressibility of glacial acetic acid is high. On adding water, the value of adiabatic compressibility decreases because of the low value of water. In different concentrations, the values are slightly different. On adding salicylic acid in to the acetic acid, the adiabatic compressibility decreases (Table III). This may lead to the presence of specific molecular interactions between the molecules of the solute and the solvent. There is an increase in acoustic impedance upon the addition of solute in to acetic acid.

Table I: *Experimental Value of Ultrasonic Velocity, Relative Density and Relative Viscosity and Computed Values of Adiabatic Compressibility, Acoustic Impedance, Relaxation Time and Attenuation of Glacial Acetic Acid at Various Temperatures.*

Temperature (ºC)	Ultrasonic velocity,C (m/s)	Relative density, ρ (kg/m^3)	Relative viscosity η (poise)	Adiabatic compressibility, $\beta x10^{10}$ (s^2/Kgm^2)	Acoustic impedance $Zx10^3$ (Kg/m^2s)	Relaxation time, $\tau x10^{-9}$	Attenuation(α/f^2) $x10^{-7}$
30	1149	1.1303	9.0822	6.7	1332.62	8.115	1.600
35	1155	1.1279	9.0777	6.64	1302.72	8.044	1.586
40	1242	1.1265	9.0831	5.75	1399.11	6.969	1.374
45	1304	1.1234	9.0764	5.23	1464.91	6.335	1.249
50	1340	1.1207	9.0745	4.96	1501.73	6.012	1.185
55	1366	1.1171	9.0669	4.79	1525.95	5.799	1.143
60	1480	1.1126	9.0532	4.1	1646.64	4.953	0.976

Table II: *Experimental Values of Ultrasonic Velocity, Relative Density and Relative Viscosity and Computed Values of Adiabatic Compressibility, Acoustic Impedance, Relaxation Time and Attenuation of Binary Mixtures of Acetic Acid and Distilled Water at Various Temperatures.*

Temperature (ºC)	Concentration (N)	Ultra sonic velocity,C (m/s)	Relative density, ρ (kg/m^3)	Relative viscosity η (poise)	Adiabatic compressibility, $\beta x10^{10}$ (s^2/Kgm^2)	Acoustic impedance $Zx10^3$ (Kg/m^2s)	Relaxation time, $\tau x10^{-9}$	Attenuation, (α/f^2) $x10^{-7}$
30	0.125	1520	1.0879	9.00583	3.97	1653.6	4.777	0.942
	0.25	1520	1.0843	8.74393	3.99	1648.13	4.653	0.917
	0.50	1522.2	1.0875	8.72247	2.3	1655	4.615	0.910
	1	1532	1.0923	8.78630	3.9	1673.4	4.569	0.901
	2	1552	1.1012	8.84788	3.77	1709.06	4.447	0.877
	3	1555.6	1.1103	8.92093	3.72	1727.18	4.27	0.873
35	0.125	1590.4	1.0826	8.90420	3.65	1721.76	4.335	0.855
	0.25	1538	1.0828	8.90580	3.9	1665.34	4.636	0.914
	0.50	1530	1.0861	8.74393	3.93	1661.73	4.585	0.904
	1	1544	1.0921	8.78900	3.84	1686.2	4.501	0.888
	2	1568	1.0986	8.85744	3.7	11768.36722.6	4.372	0.862
	3	1596	1.1080	8.91696	3.54		4.212	0.830
40	0.125	1614.4	1.0797	8.80112	3.55	1743.06	4.17	0.822
	0.25	1547.2	1.0794	8.79680	3.87	1670.04	4.563	0.891
	0.50	1542	1.0835	8.73577	3.88	1670.75	4.521	0.891
	1	1550	1.0960	8.78480	3.79	1698.8	4.448	0.877
	2	1630	1.0958	8.83480	3.43	1786.15	4.046	0.798
	3	1618	1.1050	8.90904	3.45	1787.89	4.106	0.809
45	0.125	1617.6	1.0764	8.73440	3.55	1741.18	4.134	0.815
	0.25	1554.8	1.0781	8.70980	3.83	1676.22	4.455	0.878
	0.50	1556.8	1.0811	8.73404	3.81	1683.05	4.444	0.876
	1	1582	1.0878	8.78810	3.67	1720.89	4.303	0.849
	2	1673	1.0931	8.83099	3.26	1828.75	3.848	0.759
	3	1619.2	1.1022	8.90450	3.46	1784.68	4.108	0.810

STM JOURNALS

50	0.125	1670.8	1.0726	8.68440	3.33	1792.1	3.867	0.763
	0.25	1546	1.0756	8.07069	3.88	1662.87	4.185	0.825
	0.50	1574	1.0772	8.72164	3.74	1695.51	4.357	0.859
	1	1591	1.0857	8.78087	3.63	1727.34	4.26	0.84
	2	1704	1.0901	8.82609	3.15	1857.53	3.717	0.733
	3	1806.4	1.0985	8.89410	2.78	1984.33	3.308	0.652
55	0.125	1682	1.0688	8.67420	3.3	1797.72	3.834	0.754
	0.25	1563	1.0723	8.70260	3.81	1676	4.429	0.873
	0.50	1570	1.0758	8.72109	3.77	1689.01	4.435	0.864
	1	1616	1.0823	8.78383	3.53	1748.99	4.143	0.817
	2	1732	1.0868	8.82035	3.06	1882.33	3.607	0.711
	3	1888.4	1.0947	8.88447	2.56	2067.23	3.034	0.598
60	0.125	1705.6	1.0646	8.41663	3.22	1815.78	3.623	0.714
	0.25	1647.6	1.0677	8.68680	3.45	1759.14	3.996	0.788
	0.50	1608.8	1.0704	8.70925	3.6	1722.05	4.191	0.826
	1	1628	1.0795	8.78329	3.49	1757.42	4.093	0.807
	2	1790	1.0833	8.81421	2.88	1939	3.385	0.668
	3	1961.2	1.0913	8.87390	2.38	2140.25	2.814	0.555

Table III: *Experimental Values of Ultrasonic Velocity, Relative Density and Relative Viscosity and Computed Values of Adiabatic Compressibility, Acoustic Impedance, Relaxation Time and Attenuation of Solution of Salicylic Acid in Acetic Acid at Various Temperatures.*

Temperature (ºC)	Ultrasonic velocity, C (m/s)	Relative density, ρ (kg/m^3)	Relative viscosity η (poise)	Adiabatic compressibility, $\beta x10^{10}$ (s^2/Kgm^2)	Acoustic impedance $Zx10^3$ (Kg/m^2s)	Relaxation time, $\tau x10^{-9}$	Attenuation, (α/f^2) x10^{-7}
30	1214	1.1694	.017083	5.8	1419.65	1.321	0.0026
35	1218	1.1647	.017496	5.78	1421.89	1.35	0.0027
40	1272	1.1596	.016759	5.32	1475.01	1.191	0.0023

45	1320	1.1528	.015965	4.97	1521.69	1.059	0.0021
50	1448.8	1.1490	.015743	4.14	1664.67	0.87	0.0017
55	1480	1.1431	.015462	3.99	1691.78	0.823	0.0016
60	1540	1.1379	.013887	3.7	1752.36	0.686	0.0014

The value of relaxation time is higher for glacial acetic acid than pure water. But on adding water to it and on decreasing the concentration, relaxation time becomes lesser and comparable with that of water. On adding the solute, i.e. the salicylic acid to the glacial acetic acid, the relaxation time becomes extremely small. The dispersion of ultrasonic velocity in the system should contain information about the characteristic time τ of the relaxation process that causes dispersion. The relaxation time is due to structural relaxation process [9] and in such a situation it is suggested that the molecules may be rearranged due to co-operative processes [10] (Figure 1(a–g)).

From Table II, it is clear that as the concentration of acetic acid increases, the density of the liquid increases. Density is the measure of liquid–liquid interaction. Increase in density with increase in concentration of acetic acid indicates solvent–solvent interactions while decrease in density indicates lesser-solvent interactions [11]. Also there is slight increase in the ultrasonic velocity with the concentration of acetic acid. This is because the ultrasonic velocity increases with decreasing free length and *vice versa* [12].

The computed values of acoustic parameters point to the presence of specific molecular interactions in the liquid mixtures. Hence it is concluded that the association in these mixtures is the result of hydrogen bonding in binary liquid mixtures. The observed increase of ultrasonic velocity in acetic acid + salicylic acid system is due to the solute–solvent molecular interaction. It is confirmed from the values of acoustic impedance, adiabatic compression etc. (Figure 2(a–g)).

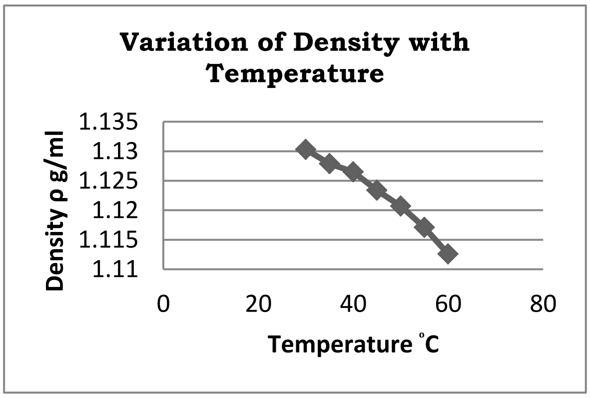


Fig 1 (a)

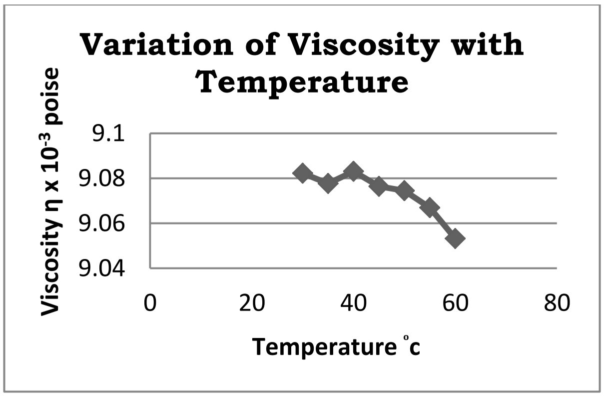


Fig 1 (b)

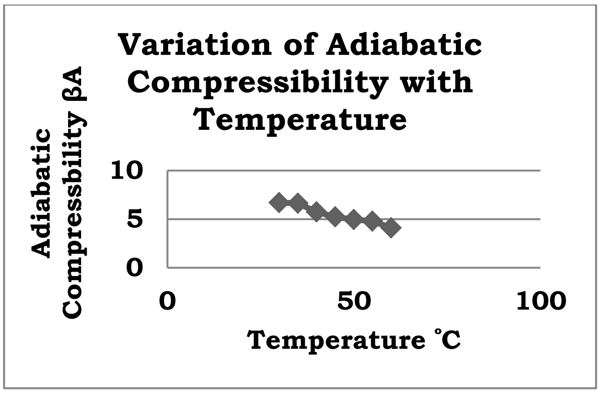


Fig 1 (c)

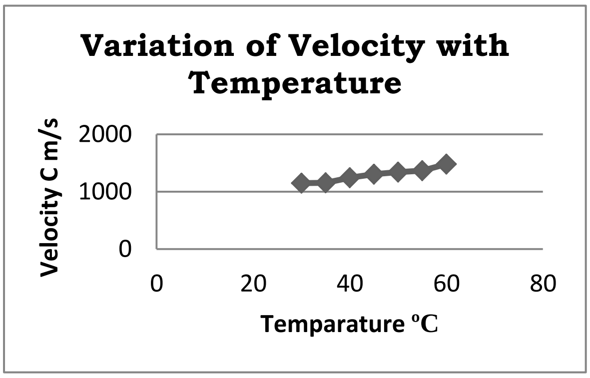


Fig 1 (d)

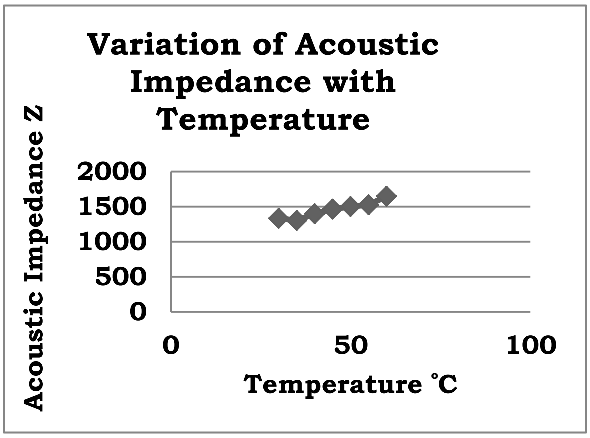


Fig 1 (e)

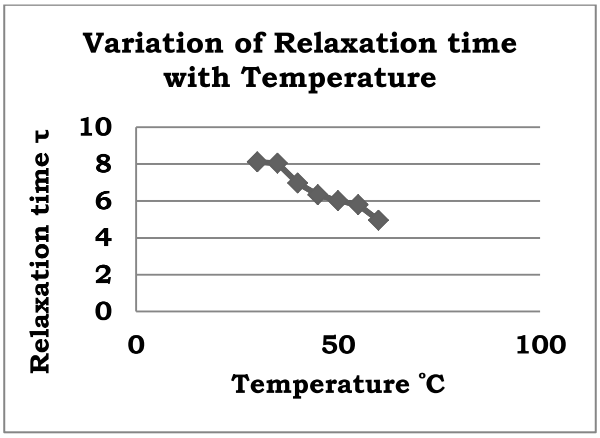


Fig 1 (f)

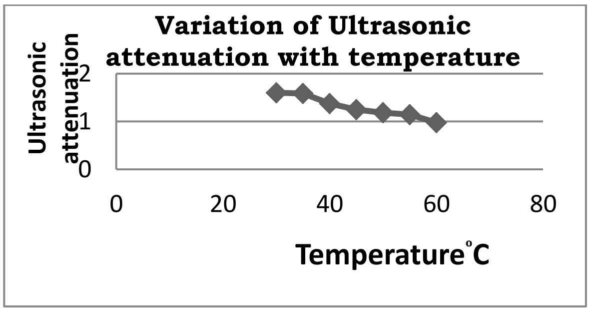


Fig 1 (g)

Fig 1 (a–g): *Variation of Relative Density, Relative Viscosity, Ultrasonic Velocity, Adiabatic Compressibility, Acoustic Impedance, Relaxation Time and Ultrasonic Attenuation of Glacial Acetic Acid with Temperature.*

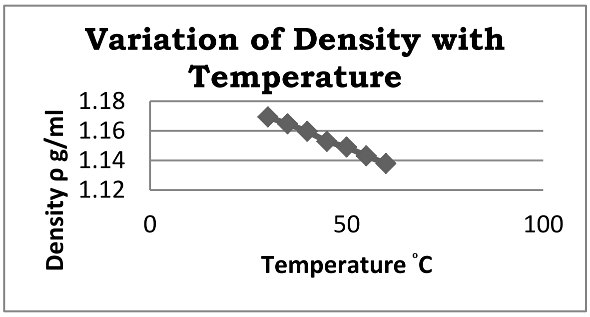


Fig 2 (a)

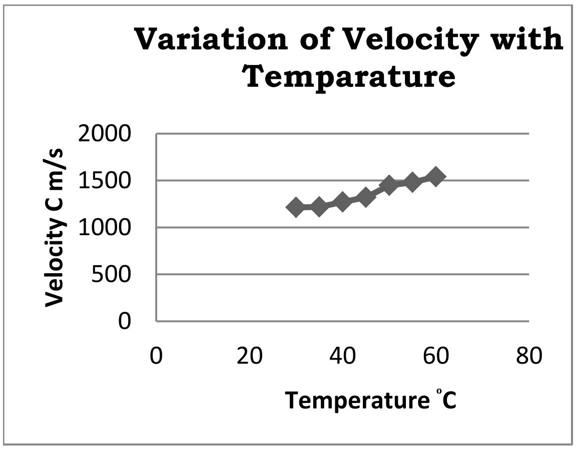
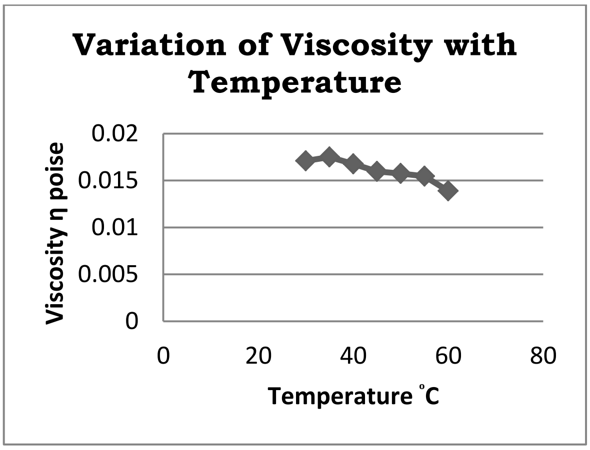


Fig 2 (b)



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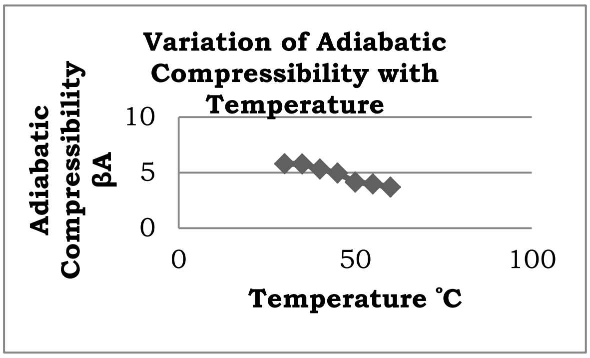

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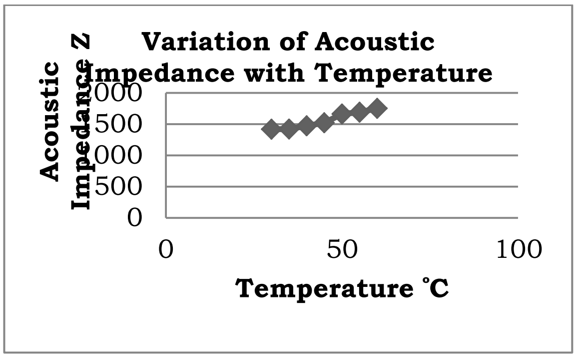

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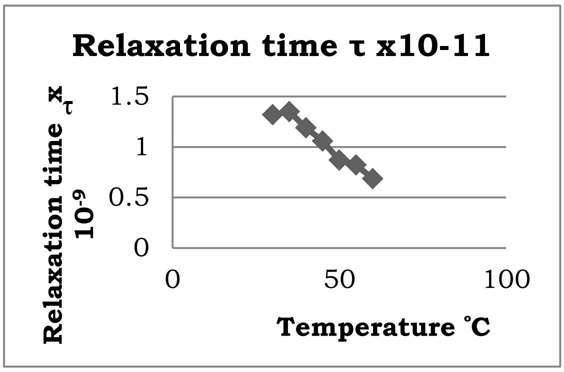

Fig 2 (f)

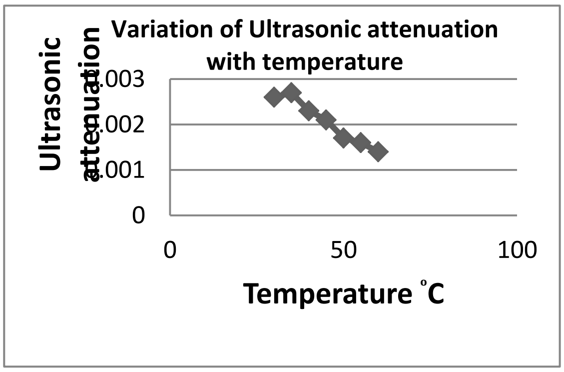

Fig 2 (g)

Fig 2 (a–g): *Variation of Relative Density, Relative Viscosity, Ultrasonic Velocity, Adiabatic Compressibility, Acoustic Impedance, Relaxation Time and Ultrasonic Attenuation of Salicylic Acid + Glacial Acetic Acid System with Temperature.*

4. CONCLUSION

The ultrasonic study was helpful for understanding the macroscopic structure of the liquids. The temperature variation affects the properties of the liquids. The nonlinear behaviour is due to the molecular interactions in the system.

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