SUMMARY

The present study has been carried out in the solvent-water mixture for substituted thiosemicarbazides and thiaoxadizines with varying concentrations of solute in the solution, change of solvent, % of solvent in water and also with varying temperatures. To study the biological effects of solutes, some solutes are arbitrarily chosen for the biological study.

The ultrasonic velocity studies at different concentration of solute indicate that the ultrasonic velocity increases with increasing concentration which happens due to increase in concentration further increasing the number of particles in a given region and in turn raising to quick transfer of sound energy. For the solutes W1 and W2 cyclic ring formation lead to the development of three bulky rings whereas for the solutes M4 and M5 the formation of cage-like structure during solute-solvent interactions suggest the H-bond forming tendency of the solute.

Among various other significant observations, it is also seen that the decrease of adiabatic compressibility and intermolecular free length supports the explanation offered for velocity variation for the solutes (M4 and M5). The contrast behaviour is observed for W1 and W2.

Intermolecular free length (Lf) depends on the intermolecular attractive and repulsive forces. As concentration increases, number of ions or particles increase in a given volume leading to decrease in the gap (intermolecular free length) between two species. Also, the decreased compressibility brings the molecules to a closer packing resulting in decrease in intermolecular free length. For the compounds M4 and M5 decrease in the intermolecular free length with the increase in ultrasonic velocity has been observed. However, for the compounds W1, W2 intermolecular free length increases with increase in concentration indicating weak intermolecular interactions.

For the compounds M4 and M5 relative association (RA) increases with increase in concentration. This increase indicates solvation of solute molecules. But, for the compounds W1 and W2 relative association decreases with increase in concentration. For the solutes M4 to M5, the Zs value also increases which indicates the interaction between the solute and solvent molecules. For W1 and W2 the Zs values decrease with concentration indicating weaker solute-solvent interactions.

The variation in all the parameters shows that solute-solvent interactions occur in both the solvent mixtures that is 85% DMSO-Water and 85% DMF-Water system. But, the strength of interaction is more in 85% DMF-Water system.

It is interesting to know that the trends of all the acoustical parameters with the increasing concentration of solutes are same in both the solvents i.e. in 85 % DMSO-Water and 85 % DMF-Water system. But, keen observations to the computed data reveals that for the solutes M4 and M5 solute-solvent interactions are much more powerful in 85 %DMF-Water system as compared to those in 85 %DMSO-Water system. However for W1, W2 and W3 the solute-solute interactions are powerful in both the solvent mixtures. Moreover, the solute M1 to M7 act as structure-promoter in both the solvent mixtures. Solutes W1 and W2 act as structure-breakers in the solvent mixtures. The difference arising in the range of solute-solvent interactions in two solvents may be because of the structural differences of DMSO-Water and DMF-Water.

It is also interesting to note that the DMSO molecules create structural effects in part because DMSO is a hydrogen bond acceptor but not donor, and in part because DMSO bonds with water. The solvated DMSO is likely to be bonded to two water molecules which strengthen the attractive force between pair of water molecules in the presence of DMSO. A study of molecular association between water and DMSO in solution indicates the presence of DMSO-Water complexes at high DMSO concentrations. Due to this, the lone pairs of solvent are not much more available to solutes for interaction. With water, DMF forms C-H----O type hydrogen bond interactions resulting in the complex H-bonded network structure of this system. The typical geometry of water pairs and characteristic of pure water is partially maintained in the mixtures. On the other hand, both the average number of water-water H-bonds and the total H-bonds per water molecule decrease with increasing DMF concentration. Hence, it can readily interact with solutes through lone pairs giving rise to large solute-solvent interaction.

For the solutes, W1 and W2 in both the solvent systems solute-solute interactions predominates because of the steric hindrance caused by the presence of extra ring of resulting in lesser penetration of solvent molecules into the solute shell.

ULTRASONIC INVESTIGATIONS IN SOME THIOSEMICARBAZIDES AND THIAOXADIZINES IN DIFFERENT CONDITIONS

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ABSTRACT: The experimental data of ultrasonic velocity, density, viscosity was obtained for some thiosemicarbazides and thiaoxadizenes in 80%, DMF over the concentration range of, (0.002 to 0.01) mol.Kg^{-1} at temperature 283 K. The derived parameters such as adiabatic compressibility (βs), free length (Lf), apparent molar volume of solute (Φ_v), limiting apparent molar volume of solute (Φ^0_v), and Jones-Dole viscosity coefficient were obtained using the density and viscosity results. The variations of these properties with concentration provided the information about the effect of concentration of solute on the solute-solvent and solvent solvent interactions. These parameters granted the information about the nature of solute and its impact on the solvent structure.

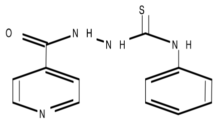
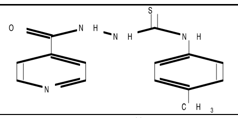
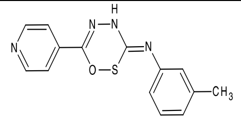
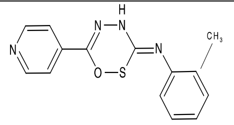
Keywords: Adiabatic compressibility, apparent molar volume, limiting apparent molar volume, apparent molar compressibility, intermolecular free length.

INTRODUCTION:

The understanding of intermolecular interactions between polar and non-polar component molecules can best be achieved by ultrasonic investigations and technological processes. Muhuri and co-workers (1996) have evaluated the apparent molar compressibility of Tetra Alkyl Ammonium Borates 1, 2 Dimethoxymethane using sound velocity measurements and the presence of solute-solute and solute-solvent interactions were predicted in the system. Jayakumar *et al.* (2001) have studied the molecular association and absorption on the electrolytic solutions of Copper Sulphate ($CuSO_4.5H_2O$) and Nickel Sulphate ($NiSO_4.5H_2O$) in water. Amalendu Pal *et al.* (2000) have made an attempt to study the speed of sound and isentropic compressibility of mixtures containing polyethers of Ethyl Acetate at 298.15 K and they discussed the dipole-dipole interaction between the components of the mixtures. Ultrasonic and sonochemical reaction studies have been carried out by measuring ultrasonic velocities in the mixing of phenols by Renga Nayakulu *et al.* (2006). They found that the reaction rate decreased due to passage of sonic waves through the medium. Such studies as a function of concentration are useful in gaining an insight into the structure and bonding of associated molecular complexes and other molecular processes. Further, they play an important role in many chemical reactions due to their ability to undergo self association with manifold internal structures (Arul and Palaniappan, 2000).

MATERIALS AND METHODS:

The solutes used in the present investigation were synthesized by standard method as reported by the earlier workers (*Berad et al.,2002)*. Solvents 80% DMF-Water was prepared using DMF of analytical grade and double distilled water. These chemicals were obtained from E. Merck. All solvents were used after purification by distillation. The temperature was maintained by a thermostatically controlled water bath LTB-10. The density of the solutions has been measured at 10 °C (283K) by the hydrostatic plunger method. A monopan digital balance of least count 0.0001g was used to record change in plunger weight dipped in solutions. The viscosities were calibrated with doubly distilled water, 80% DMF-Water. Care was taken to reduce evaporation during the measurements. A thoroughly cleaned and dried Ostwald viscometer filled with experimental liquid was placed vertically in a glass-fronted, well-stirred water bath. After thermal equilibrium was attained, the flow times of the liquid were recorded with an accurate stopwatch (±0.01s). The present value for the liquid agrees with the literature value within a deviation of the order of 0.01 poise. Ultrasonic velocity measurements were made by variable path single crystal interferometer (Mittal Enterprises, Model F-81) at 2 MHz with accuracy of ±0.03 %. The folowing solutes are used in the present paper:

S. no.	Name of the Solute	Structural Formula
M1	1-γ-picolinoyl-4-phenyl thiosemicarbazide	
M2	1-γ -picolinoyl-4-p-tolyl thiosemicarbazide	
W1	3-[pyrid-4yl]-5H-6-m-tolylimino-1,2,4,5 thiaoxadiazine	
W2	3-[pyrid-4yl]-5H-6-tolylimino-1, 2, 4, 5 thiaoxadiazine	

RESULTS AND DISCUSSIONS :

Ultrasonic Velocity (U): Sound is a vibration that travels through an elastic medium as a wave. The speed of sound describes how far this wave travels in a given amount of time. Ultrasonic velocities are incorporated in Table−1, for solutes M1, M2, W1 and W2. In case of M1and M2, sound velocity increases with increase in concentration of solute. Earlier workers have reported the similar increase in velocity with increase in concentration of different solutes (Rajagopalan *et al.*, 2002; Srilalitha *et al.*, 1996). The increase suggests a structure-making capacity of these solutes in solution.

EXPERIMENTAL AND COMPUTED DATA:

Conc. (kg mol^{-1})	Us (ms^{-1})	βs x 10^{-10} (m^{2}N^{-1})	Lf (A^0)	RA	τ x 10^{-6} (s)	Φ_k x 10^{-3} (m^{2}N^{-1})	Φ_v (m^{3}mol^{-1})	Zs (kgm^{-2}s^{-1})
M1								
0.010	1696.9	2.3815	32.1360	1.8027	18.1733	98.3011	−71.7507	1959.5271
0.008	1691.1	2.5208	41.1196	1.6930	17.9328	24.6166	−76.2123	1933.4102
0.006	1683.7	2.6657	52.2332	1.6895	17.6325	22.3516	−85.9074	1915.5043
0.004	1680.0	2.7162	61.5166	1.5844	16.6725	20.6196	−105.7075	1905.5546
0.002	1679.2	3.0193	66.0148	1.4343	15.6518	17.2035	−121.2051	1776.7581
M2								
0.010	1712.8	2.3848	72.1235	1.8001	20.3599	87.0633	−117.8593	1942.6111
0.008	1698.5	2.4896	76.5129	1.6933	19.0480	22.9489	−118.1281	1925.1960
0.006	1670.0	2.6068	83.0032	1.6918	18.9568	21.2266	−123.0752	1898.3205
0.004	1666.8	2.6887	84.1478	1.5473	17.9469	20.1233	−122.8750	1839.8106
0.002	1657.9	2.9698	85.1023	1.4452	15.9907	19.4525	−156.3751	1798.6912
W1								
0.010	1498.5	4.2074	91.2031	1.4218	17.3087	55.1423	107.1672	1410.2140
0.008	1651.7	3.1504	87.6237	1.4408	17.4121	79.5982	105.9432	1667.1480
0.006	1717.0	2.9499	74.3528	1.4509	17.5217	107.8737	86.9991	1743.5830
0.004	1733.4	2.7041	62.5042	1.4984	17.8007	115.1841	86.9091	1856.2951
0.002	1739.2	2.6965	50.0493	1.5077	18.9673	428.2987	65.9665	1882.5752
W2								
0.010	1507.4	4.1883	92.9119	1.2846	18.1604	47.0490	113.4415	1504.0940
0.008	1631.2	3.3805	85.5716	1.3263	18.3511	51.3181	112.8340	1554.9921
0.006	1706.5	2.9292	75.6811	1.4212	18.6332	70.3971	85.6018	1733.3853
0.004	1722.9	2.8732	63.5022	1.5000	18.9171	98.7145	85.8018	1761.5421
0.002	1728.7	2.6877	45.7213	1.5073	20.4161	415.3811	66.4183	1863.6520

Moreover, the increase in ultrasonic velocity indicates the possibility of H-bond formation between solute and solvent. There is also an indication of greater association among the molecules. The contrast behaviour was observed for the compounds W1, W2 where ultrasonic velocity decreases with concentration. This suggests weaker solute-solvent interactions for these solutes. It indicates the structure-breaking tendency of the solutes. The association between the molecules in W1, W2 is weaker in comparison to the compounds M1 to M2.

The difference occurs perhaps due to the cyclic ring formation in W1, W2. This leads to the formation of three bulky rings which may result in steric hindrances resulting in weaker interaction between solute and solvent.

Adiabatic Compressibility (βs): It is a measure of intermolecular association or repulsion calculated from the measured ultrasonic velocity (Us) and density (d). The deviation in adiabatic compressibility can be explained (Ravichandran and Ramanathan, **2010)** by taking into consideration the following factors:

1) Loss of di-polar association and difference in size and shape of the component molecules lead to decrease in velocity and increase in compressibility.

2) Dipole-dipole interaction or hydrogen bonded complex formation between unlike molecules leads to increase in sound velocity and decrease of compressibility. The actual deviation depends on the resultant effect.

The compressibility data indicates that as more and more solute molecules are added, it attracts more solvent molecules towards itself and less number of solvent molecules is available for incoming species. As a result of this, the adiabatic compressibility decreases with the increase in concentration.

The contrast behaviour is observed for W1, W2 where adiabatic compressibility increases with increase in concentration of solute which again supports the observation that interaction are weak in these compounds.

Intermolecular Free Length (Lf): Adiabatic compressibility is inversely related to density whereas free length is directly related to adibatic compressibility. Hence, Lf is inversely related to density. Hence ion-solvent interactions increase. As ion-solvent interaction increases it leads to smaller electrical conductivity. The similar findings are of earlier authors **(Idrees** ***et al.*****, 2003)**. The decreased compressibility brings the molecules to a closer packing resulting in decrease in intermolecular free length. For the compounds M1 and M2 a decrease in the intermolecular free length with the increase in ultrasonic velocity has been observed. The variation of intermolecular free length with concentration is shown in TableI. But for the compounds W1 and W2 intermolecular free length increases with increase in concentration indicating weak intermolecular interactions. There is a decrease in the hydrogen bonding interaction in water. Hence, the free length is seen to be increasing.

Relative Association (RA): Relative association denotes magnitude of the associations. The relative association is influenced by breaking up of the solvent molecules on addition of solute to it and subsequent solvation of ions by the free solvent molecules. The former effect results in a decrease while the later increases the values of relative association (**Ali** ***et al.*****, 2001)**. It depicts that for the compounds M1 and M2 relative association (RA) increases with increase in concentration. This increase indicates solvation of solute molecules. A similar increase in the value of RA has been found in case of sucrose solution by Syal *et al.* (***1998)***. But for the compounds W1and W2 relative association decreases with increase in concentration. This indicates the breaking up of the associated solvent molecules on addition of solute. This indicates the structure-breaking tendencies of solutes.

Viscous Relaxation Time (t): The linear variation of relaxation time in the whole concentration range may be taken as the absence of every solute-solute molecular association in the solution. On the other hand, the non-linear variation of the relaxation time is interpreted as possible solute-solute molecular association which has been observed in the present study. Kalyanasundaram *et al*. **(1995)** also reported the increase in relaxation time due to interaction between polymethyl methacrylate and chlorobenzene.

Apparent molar compressibility (F_k): As apparent molar compressibility (F_k) depends on adiabatic compressibility which in turn depends on concentration, it can be said that apparent molar compressibility (F_k) is related to concentration. It represents the magnitude of ion-solvent interaction.

Apparent molar volume (F_v)**:**The apparent molal volume is another important acoustical parameterto understand solute-solvent and solute-solute interactions. From TableI it is observed that for M1 and M2 the F_v values are negative that indicates the structure-making tendency of the solutes. The solutes W1and W2 possess positive F_v indication of structure-breaking tendency of the solute. This occurs because solute gets dissolved preferentially in the non-lattice component of solvent, thereby shifting the equilibrium from lattice to non-lattice and destroying some range of solvent structure.

Specific acoustic impedance (Zs): When the sound wave travels through a solution, certain part of it is absorbed in the medium and rest gets reflected by the ion (Thirumaran and Sabu, 2009; Selvakumar, Krishna Bhat, 2008) that is restriction for the free flow of sound velocity by the ions. The character that determines this restriction or backward movement of sound waves is known as acoustic impedance. It is also regarded as one of the parameter to ascertain the formation of heterogeneous molecular complex in liquid mixtures. Acoustic impedance is dependent on molecular geometry and is complicated by the fact that the velocity and pressure are not necessrlily in phase but exhibit efficient transfer of sound energy from point to point and therefore serves further to describe solvent behaviour in altogether different perspective (Bhatnagar *et al.*, 2010).

From the data given in Table–I, it is evident that Zs increases with increase in concentration of solute M1 amd M2. This is in agreement with the theoretical requirements as velocity and density both increase with increasing concentration of solute in solution. The increase of Zs values with solute concentration can be attributed to the powerful solute-solvent interactions. The same findings have been noticed by earlier researchers *(Agrawal et al., 2011)*.

ACKNOWLEDGEMENT:

The authors acknowledge with thanks the support of the Principal, Head of Department and Director of Dr. I. N. Nimdeokar P. G. & Research Centre for Chemistry, Hislop College Nagpur.

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International Journal of Researches In Biosciences, Agriculture & Technology
Feb. 2015,
Special Issue (2)
ISSN No. (Online) 2347-517X

Molecular interactions of substituted thiosemicarbazides and thiaoxadizenes in dimethylformamide and dimethylsulphoxide

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ABSTRACT

The experimental data of ultrasonic velocity, density, viscosity have been obtained for some thiosemicarbazides and thiaoxadizenes in 85% DMSO over the concentration range of, (0.002 to 0.01) mol.Kg^{-1}. The derived parameters such as adiabatic compressibility (βs), apparent molar volume of solute (Φv), limiting apparent molar volume of solute (Φ^0v), and Jones-Dole viscosity coefficient were obtained using the density and viscosity results. The variations of these properties with concentration give the information about solute-solvent interactions.

Key words: Ultrasonic velocity, adiabatic compressibility, (βs), Apparent Molar Compressibility (Φ_k), Apparent Molar Volume (Φv), limiting apparent molar volume (Φ^0v)

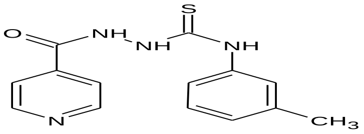
INTRODUCTION

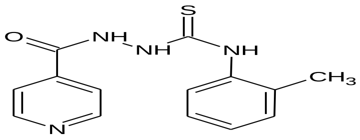
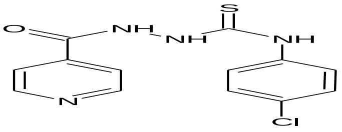
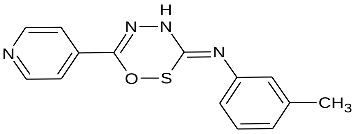
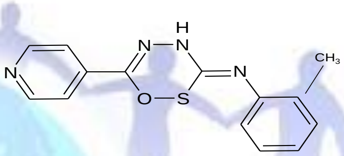
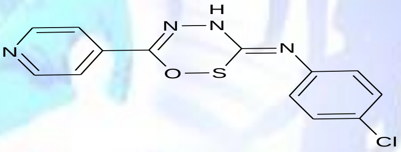
In the recent years, measurements of the Ultrasonic velocity are helpful to interpreted solute-solvent, ion solvent interaction in aqueous and non-aqueous medium[1-4]. Jahagirdar[5] et. al. has studied the acoustical properties of four different drugs in methanol and he drawn conclusion from adiabatic compressibility. The four different drugs compress the solvent methanol to the same extent but it shows different solute-solvent interaction due to their different size, shape and structure. Meshram[6] *et. al.* studies the different acoustical properties of some substituted Pyrazolines in binary mixture acetone-water and observed variation of ultrasonic velocity with concentration. Palani[7] have investigated the measurement of ultrasonic velocity and density of amino acid in aqueous magnesium acetate at constant temperature. The ion-dipole interaction mainly depends on ion size and polarity of solvent. The strength of ion-dipole attraction is directly proportional to the size of the ions, magnitude of dipole. But inversely proportional to the distance between ion and molecules. Voleisines[8] have studied the structural properties of solution of lanthanide salt by measuring ultrasonic velocity..Tadkalkar[9] *et. al.* have studied the acoustical and thermodynamic properties of citric acid in water at different temperature. Mishra[10] et.al. have investigated ultrasonic velocity and density in non aqueous solution of metal complex and evaluate acoustic properties of metal complex.

MATERIALS AND METHOD

The solutes used in the present investigation were synthesized by standard methods as reported by the earlier workers[11]. The solvent DMSO used was of analytical grade. It was obtained from E. Merck Chemical Company. Solvent was used after purification by distillation. Double distilled water was used for preparing the 85% DMSO-Water system. The temperature was maintained by a thermostatically controlled water bath LTB−10. The density of the solution was measured at 10 °C (283 K) by the hydrostatic plunger method. A mono-pan digital balance of least count 0.0001g was used to record change in plunger weight dipped in solutions.

A thoroughly cleaned and dried Ostwald viscometer filled with the experimental liquid was placed vertically in a glass-fronted, well-stirred water bath. Once the thermal equilibrium was attained, the flow times of the liquid were recorded with an accurate stopwatch (±0.01s). The viscosities were calibrated with double distilled water and with DMSO. Care was taken to reduce evaporation during the measurements. The present value for the liquids agrees with the literature value within a deviation of ±0.01 poise. Ultrasonic velocity measurements were made by variable path single crystal interferometer (Mittal Enterprises, Model F–81) at 2MHz with the accuracy of ±0.03 %. The following compounds are taken for study:

M3	1- γ -picolinoyl-4-m-tolyl thiosemicarbazide	

M5	1- γ -picolinoyl-4-o-tolyl thiosemicarbazide	
M7	1- γ -picolinoyl-4-p-Chloro phenyl thiosemicarbazide	
W1	3-[pyrid-4yl]-5H-6-m-tolylimino-1,2,4,5 thiaoxadiazine	
W2	3-[pyrid-4yl]-5H-6- o-tolylimino-1, 2, 4, 5 thiaoxadiazine	
W3	3-[pyrid-4yl]-5H-6-p-chloro phenyl imino-1,2,4,5 thiaoxadiazine	

EXPERIMANTAL AND COMPUTED DATA

Table I: Values of Velocity (Us), Viscosity (ηs), Adiabatic Compressibility (βs), Apparent Molar Compressibility (Φ_k) and Apparent Molar Volume (Φv) for all solutes in 85% DMSO−Water system at 283K.

Conc. (kg mol^{-1})	Us (ms^{-1})	ηs x10^{3} (Nsm^{-2})	βs x10^{-10} (m^{2}N^{-1})	Φ_k x10^{-3} (m^{2}N^{-1})	Φv (m^{3}mol^{-1})
M3					
0.010	1708.1	3.8894	3.3814	55.6930	-80.826
0.008	1707.0	3.7366	3.4974	39.0166	-111.4349
0.006	1704.6	3.2773	3.6841	28.6409	-122.6196
0.004	1702.0	3.2201	3.7140	20.0118	-140.2817
0.002	1638.2	2.9630	4.3384	5.7668	-207.4526
M5					

0.010	1960.6	5.5215	2.1109	93.7886	−49.2751
0.008	1680.2	4.6193	3.0602	86.1484	−90.8401
0.006	1655.8	4.3966	3.1772	73.3427	−121.3462
0.004	1643.7	4.3191	3.2572	65.0098	−124.7535
0.002	1641.6	4.0590	3.8076	21.2986	−157.3262
M7					
0.010	1716.6	3.8812	3.1171	95.4134	−43.0835
0.008	1713.6	3.5338	3.1280	91.2177	−50.3584
0.006	1710.6	3.1958	3.1391	80.4963	−56.3806
0.004	1704.2	3.0517	3.1626	76.3710	−65.5931
0.002	1698.2	2.6656	3.1852	31.5056	−78.1796
W1					
0.010	1483.7	2.8767	4.8474	50.5423	55.6665
0.008	1636.9	3.1097	3.7104	72.4982	76.1091
0.006	1702.2	3.3140	3.4099	99.5737	84.0679
0.004	1718.6	3.7457	3.1710	110.8840	96.3432
0.002	1724.4	3.8330	3.1165	123.6987	98.4672
W2					
0.010	1483.7	2.8632	4.8703	40.6490	52.2183
0.008	1636.9	3.0685	3.9825	42.4181	71.1018
0.006	1702.2	3.5214	3.4312	60.2971	85.1243
0.004	1718.6	3.5508	3.3452	87.6145	99.3340
0.002	1724.4	3.7926	3.1497	103.981	100.8415
W3					
0.010	1413.1	2.8080	5.3841	37.8825	68.8870
0.008	1426.2	2.8764	5.2481	53.3142	71.9072
0.006	1465.0	3.2162	4.8919	60.1445	83.5487
0.004	1489.5	3.3591	4.6616	75.1863	89.3421
0.002	1492.7	3.5157	4.5387	79.6615	96.0489

Table–II: Values of intercept (A), slope (B), limiting molar compressibility (Φ^0_k), slope (S_k), limiting molar volume (Φ^0_v), slope (S_v) for different solutes in 85% DMSO-Water system at 283 K.

Solutes	A $(dm^3mol^{-1})^{1/2}$	B (dm^3mol^{-1})	Φ^0_k x 10^{-3} (m^2N^{-1})	S_k x 10^{-3} $(N^{-1}m^{-1}mol^{-1})$	Φ^0_v (m^3mol^{-1})	S_v $(m^3kg^{-1/2}mol^{-3/2})$
M3	−2.1023	1.2451	0.8552	−0.0342	2101.3673	−290.0711
M5	−2.3145	1.2056	1.2504	−0.0258	1780.5836	−242.2054
M7	−2.1065	1.2802	1.0867	−0.0064	626.7442	−105.7085
W1	2.1056	−1.2316	−1.3096	0.1896	−741.8527	137.7503
W2	2.2316	−1.2489	−1.2627	0.1616	−880.6812	147.7520
W3	2.0060	−1.2640	−0.7509	0.1175	−518.0371	120.7860

RESULTS AND DISCUSSION

Ultrasonic Velocity (U): The ultrasonic velocity, 'U' depends on the wavelength 'λ' of the sound wave. Since the frequency (2 MHz) is constant, λ increases with the increase in the concentration as depicted in Table−I. Hykes *et al.*[12] reported that the ultrasonic velocity in medium depends inversely on density and adiabatic compressibility of the medium. For the compounds M3, M5 and M7 data reveals increase in ultrasonic velocity (U) with increase in the concentration of solute. This suggests presence of solute-solvent interactions[13-14]. The increase suggests a structure-making capacity of these solutes in solution. Moreover, the increase in ultrasonic velocity indicates the possibility of H-bond formation between solute and solvent. There is also an indication of greater association among the molecules.

The contrast behaviour was observed for the compounds W1, W2 and W3 where ultrasonic velocity decreases with concentration. The results are in accordance with earlier findings[15]. This suggests weaker solute-solvent interactions for these solutes. It indicates the structure-breaking tendency of the solutes. The association between the molecules in W1, W2 and W3 is weaker in comparison to the compounds M3, M5 and M7. The difference occurs perhaps due to the cyclic ring formation in W1, W2 and W3. This leads to the formation of three bulky rings which may result in steric hindrances resulting in weaker interaction between solute and solvent.

Viscosity (η): Viscosity of a solvent or solution is a measure of cohesiveness or rigidity present in between either solute-solute or solute-solvent or solvent-solvent molecules in a solution. As density and viscosity of any solution or solvent are directly related to each other, the measured values show similar trend. From the computed data given in Table-I, for the solutes M3, M5 and M7 viscosity increases with concentration of solute. This may be due to the formation of cage like structure during solute-solvent interactions. Again the increase suggests the H-bond forming tendency of the solute. The solutes are of structure-maker type. Viscosity data were analysed in the light of Jones-Dole equation [15].

$$\eta / \eta_o = 1 + AC^{1/2} + BC$$

which can be written as $[\eta / \eta_o - 1] / \sqrt{C} = A + BC^{1/2}$

where A and B are the Falkenhagen and Jones-Dole Coefficients. Others are with usual notations. Here A (i.e. intercept gives the value of magnitude of solute-solute interaction) and B (i.e. slope gives the value of magnitude of solute-solvent interaction) have been computed by the least square method from the linear plot of $[\eta / \eta_o - 1] / \sqrt{C}$ Vs $\sqrt{C}$ and are tabulated in Table−II. The increase in viscosity is due to the presence of particles arises from the fact that they lie across the fluid stream lines and are subject to torrisional force[16-17]. They tend to rotate and absorb energy. This energy absorption corresponds to an increased viscosity for the solution. But W1, W2 and W3 show decrease in viscosity which may be due to steric effect. So, on increasing the concentration, interactions are weakened. For the compounds M3, M5 and M7 the values of A are negative and B are positive. Since A is a measure of long range interionic forces[18-20] it is evident that there is a weak solute-solute interaction in the systems studied. B-Coefficient is known as a measure of solute-solvent interaction and is directly dependent on the size and shape of the solute molecules. It is a measure of the effective hydrodynamic volume of solvated ions/solute which accounts for the ion-solvent interactions. It is also known as a measure of order or disorder introduced by the ions or solute into the solvent. In compounds W1, W2 and W3 the trend is reverse, here A values are positive indicating the absence of long range interionic forces. B values are negative which indicates the structure-breaking tendencies of the solutes.

Adiabatic Compressibility (βs): From the computed data it has been observed that for the compounds M3, M5 and M7 the adiabatic compressibility decreases with increase in concentration of solute. This may be due to the aggregation of solvent molecules around the ions supporting solute-solvent interaction. The results are in accordance with the findings of earlier authors[21-22]. As concentration increases, a larger portion of the water molecules are electrorestricted and the amount of bulk water decreases causing the compressibility to decrease. Decrease in adibatic cmpressibility indicates the formation of large number of tightly bound systems.

The contrast behaviour is observed for W1, W2 and W3 where adiabatic compressibility increases with increase in concentration of solute which again supports the observation that interaction are weak in these compounds. These findings are in accordance with the earlier one [23].

Apparent Molar Compressibity (Φ_k):

Apparent molar compressibity Φ_k, was calculated by using the following equation [24-25]:

$$\Phi_k = [(1000\,(d_o\beta s - ds\ \beta_0)/C\ do\ ds] + [\beta s\ M/ds].$$

The calculated values are shown in Table–I. In the above equation, all the terms are constant, except concentration C and compressibility βs. Hence, Gucker[26] suggested the equation, $\Phi_k = \Phi^0_k + S_k C^{1/2}$ on the basis of Debye–Huckel theory. The limiting molar compressibility Φ^0_k and the slope S_k are shown in Table–II. S_k and Φ^0_k represent the measure of solute-solute and solute-solvent interactions[27] respectively.

The comparative high values of Φ^0_k for solutes M3, M5 and M7 may be due to local compressibility of solvent near solute. Solute-solvent interaction predominates solute-solute interaction which is refllected from the lower values of S_k. However, for W1, W2 and W3 lower values of Φ^0_k and higher values of S_k shows that solute-solute interaction predominates the solute-solvent interactions.

Apparent Molar Volume ((Φ_v): Apparent molar volume Φ_v, is the practically available molar volume of the solute, that is molar volume of the solute density per unit concentration[28–29]. This was calculated using the following equation:

$$\Phi_v = (M/ds) + [\ 1000\ [(do - ds]/Cdsdo$$

In above equation, all the terms are constant for a given system, except the concentration and density. These two are interrelated by the linear equation $\Phi_v = \Phi^o_v + Sv\ C^{1/2}$, proposed by Masson[30]. Φ^o_v gives the information about solute-solvent interactions. Table−II reveals for the solutes M3, M5 and M7, Φ^0_v values are positive and large, indicating the presence of strong solute-solvent interactions. But for W1, W2 and W3, Φ^0_v values are negative indicating stronger solute-solute interactions which may be due to steric hindrance because of presence of extra ring which resist the penetration of solvent molecules into the solute shell.

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