ACOUSTICAL STUDIES OF SOME THIOSEMICARBAZIDES AND THIAOXADIZINES IN DIFFERENT PERCENTAGE OF SOLVENTS

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Abstract

The experimental data of ultrasonic velocity, density, viscosity have been obtained for some thiosemicarbazides and thiaoxadizenes in 80% , DMF in 85% DMF and in 90% DMF over the concentration range of, (0.002 to 0.01) mol.Kg^{-1}. The derived parameters such as adiabatic compressibility (βs), free length (Lf), apparent molar volume of solute (Φv), limiting apparent molar volume of solute ($\Phi^0 v$), 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.

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

1. Introduction

Modelling of solvent effects is one of the most useful methods to obtain information about the mechanism of organic reactions. During the last few years, special attention is being paid towards study of solvent effects on different reactions as mentioned by researchers [1–6]. A solvent would provide not only a background for the reaction to occur but would stabilize the reactants and the transition state by solvating them. This solvation is due to solvent-solute interactions during which a solvent can act either as a nucleophile or an electrophile by donating or accepting electron pairs from the solute. It can also form hydrogen bonds with the specific sites of the solute molecules.

According to Gholami [7] solvent-solute interactions are much more complex in mixed solvents than in pure solvents due to the preferential solvation by any of the components present in the solvent mixture. Due to this, the local composition of the solvent shell will be different from that in the bulk as Marcus and others have observed [8–10]. In addition to this in binary solvent mixtures, the solvent-solvent interactions dominate the solute-solvent interactions since solvent is present in large excess compared to solute. These solvent-solvent interactions may be due to hydrogen bond formation or due to dipolar effects, which would affect the property under consideration. Thus, by studying any solvent dependent property in binary solvent mixtures one can get an idea about inter-solvent interactions. With this view, these solvent-solvent and solvent-solute interactions have been estimated.

2. Materials and Methods

The solutes used in the present investigation were synthesized by standard methods as maintained by Bhaskar [11]. These are 1- γ -picolinoyl-4-t-butyl thiosemicarbazide (M6), 1- γ -picolinoyl-4-p-Chloro phenyl thiosemicarbazide (M7), 3-[pyrid-4yl]-5H-6-m-tolylimino-1,2,4,5 thiaoxadiazine (W1) , 3-[pyrid-4yl]-5H-6- o-tolylimino-1, 2, 4, 5 thiaoxadiazine (W2). The solvent DMF 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 different percentage of DMF-water system. 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 ($\pm$0.01s). The viscosities were calibrated with double distilled water and with DMF. Care was taken to reduce evaporation during the measurements. The present value for the liquids agrees with the literature value within a deviation of $\pm$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 $\pm$0.03 %. Ultrasonic and thermodynamic parameters have been measured at 10°C (283K).

S.No	Solutes	Structure
1	1- γ-picolinoyl-4-t-butyl thiosemicarbazide (M6)	
2	1- γ-picolinoyl-4-p-Chloro phenyl thiosemicarbazide (M7)	
3	3-[pyrid-4yl]-5H-6-m-tolylimino-1,2,4,5 thiaoxadiazine (W1)	
4	3-[pyrid-4yl]-5H-6- o-tolylimino-1, 2, 4, 5 thiaoxadiazine (W2)	

3. Theory and Formulae

The Apparent Molal Volumes (ϕ_v) and Apparent Molal Adiabatic Compressibilities (ϕ_k) in solutions are determined respectively from Density (ds) and Adiabatic Compressibility (βs) of solution using the equations:

$$\phi_v = (M/ds) + [(do - ds)10^3] / C\ ds\ do \qquad \ldots \ldots \ldots (1)$$

$$\phi_k = [1000 (\beta s\ do - \beta o\ ds) / C\ ds\ do] + (\beta s\ M /ds) \qquad \ldots\ldots\ldots(2)$$

where, 'do' is the density of pure solvent; 'C' is Molality expressed in Mol Kg^{-1}; 'M' is the molecular Weight of Solute; 'βo' is adiabatic compressibility of pure solvent and 'βs' is adiabatic compressibility of solution, calculated using the equations:

$$\beta s = 100 / (Us^2 ds) \quad \ldots (a) \quad \text{and} \quad \beta o = 100 / Uo^2\, do \quad \ldots (b)$$

Where, 'Us' is the ultrasonic velocity in the solution in m/s; 'βs' is in bar^{-1} and 'φ$_k$' is in cm^3 mol^{-1} bar^{-1}. The values of 'φ$_k$' and 'φ$_v$' were plotted versus √C.

$$\phi_v = \phi^0_v + S_v \sqrt{C} \qquad \ldots \ldots \ldots (3)$$

$$\phi_k = \phi^0_k + S_k \sqrt{C} \qquad \ldots \ldots \ldots (4)$$

Where, 'φ^0_v and φ^0_k' are the limiting molar volumes and limiting molar adiabatic compressibilities respectively. 'S$_v$' and 'S$_k$' are the experimental slopes representing 'ion-ion interactions'.

The Intermolecular free length (Lf), Specific acoustic impedance (Zs) and Relative Association (RA) are calculated by using the following equations:

$$Lf = K \times \sqrt{\beta s} \qquad \ldots \ldots \ldots (5)$$

$$Z = Us \times ds \qquad \ldots \ldots \ldots (6)$$

$$RA = (ds \times Uo) / (do \times Us) \qquad \ldots \ldots \ldots (7)$$

From the graph of 'φ$_k$' versus '√C, φ^0_k' (Thermodynamic Parameter i.e., limiting Molar adiabatic compressibility) at zero mole fraction can be evaluated. Viscous relaxation Time 'τ' was calculated using the equation;

$$\tau = 4\eta / 3\, ds \times Us^2 \qquad \ldots \ldots \ldots (8)$$

The solvation number (Sn) was calculated using the equation;

$$Sn = - (\phi_k / \beta o \times M \times do) \qquad \ldots \ldots \ldots (9)$$

4. Results and Discussion

Table I: Velocity (Us), Adiabatic Compressibility (βs), Intermolecular Free Length (Lf), Relative Association (RA), Viscous Relaxation Time (τ), Apparent Molar Compressibility (Φ_k), Apparent Molar Volume (Φ_v) and Specific Acoustic Impedance (Zs) Of M6 in Different Concentrations and Different Percentages of DMF-Water at 10 °C (283K).

Conc. (kg mol⁻¹)	Us (ms⁻¹)	βs x 10⁻¹⁰ (m²N⁻¹)	Lf (A⁰)	RA	τ x 10⁻⁶ (s)	Φ_k x 10⁻³ (m²N⁻¹)	Φ_v (m³mol⁻¹)	Zs (kgm⁻²s⁻¹)
80% of DMF – Water								
0.010	1725.0	2.6934	31.4619	1.7107	21.6395	98.7823	−90.1671	1746.2308
0.008	1723.9	2.8894	40.4829	1.5812	20.8304	87.2155	−120.7491	1691.0003
0.006	1721.5	3.1761	41.7219	1.5384	19.6998	76.3210	−125.6872	1608.5112
0.004	1718.9	3.2361	51.9519	1.4345	18.8516	75.7918	−125.4871	1598.2916
0.002	1655.1	3.8704	58.5721	1.2797	17.0409	24.9171	−143.1560	1424.6003
85% of DMF – Water								
0.010	1719.4	3.3934	35.3619	1.0107	18.5395	88.4222	−82.4671	1736.0380
0.008	1718.3	3.5094	45.9829	0.9812	18.4304	82.5155	−123.9491	1680.0031
0.006	1715.9	3.6961	47.5219	0.9384	17.0998	71.4210	−125.7970	1597.3223
0.004	1713.3	3.7261	58.5519	0.9345	16.9516	70.8918	−129.8872	1586.1964
0.002	1649.5	4.3504	65.6721	0.8797	16.1409	17.7171	−147.0563	1412.1031
90% of DMF – Water								
0.010	1700.3	3.5312	37.1456	1.0023	17.1658	78.1036	−93.1456	1725.3623
0.008	1713.3	3.6136	48.9132	0.9712	17.0098	77.1362	−125.1236	1677.1032
0.006	1700.8	3.7013	47.9878	0.9213	16.9230	73.4898	−128.6231	1568.6210
0.004	1709.8	3.8023	59.1231	0.9145	16.1562	63.4236	−131.2368	1575.2036
0.002	1631.2	4.5316	66.1023	0.8613	16.0097	12.4895	−149.4562	1400.2310

Table II: Velocity (Us), Adiabatic Compressibility (βs), Intermolecular Free Length (Lf), Relative Association (RA), Viscous Relaxation Time (τ), Apparent Molar Compressibility (Φ_k), Apparent Molar Volume (Φ_v) and Specific Acoustic Impedance (Zs) of M7 in Different Concentrations and Different Percentages of DMF–Water at 10 °C (283K).

Conc. (kg mol⁻¹)	Us (ms⁻¹)	βs x 10⁻¹⁰ (m²N⁻¹)	Lf (A⁰)	RA	τ x 10⁻⁶ (s)	Φk x 10⁻³ (m²N⁻¹)	Φv (m³mol⁻¹)	Zs (kgm⁻²s⁻¹)
80% of DMF – Water								
0.010	1732.0	2.4311	43.5109	1.9561	20.1596	99.4134	−47.9835	1838.2121
0.008	1729.0	2.5220	44.7815	1.7857	18.4891	97.7177	−54.3584	1752.9150
0.006	1726.0	2.6331	52.8308	1.7797	17.7647	91.1963	−68.5931	1723.2680
0.004	1719.6	2.6866	62.8408	1.6626	16.9253	85.0711	−68.3931	1711.1210
0.002	1713.6	2.7192	73.1521	1.5131	14.9239	40.5056	−81.4796	1605.5061
85% of DMF – Water								
0.010	1726.4	3.1311	47.4109	1.2561	17.0596	89.5413	−40.2835	1828.0121
0.008	1723.4	3.1421	47.8311	1.1857	16.0891	93.0177	−57.5584	1741.9150
0.006	1720.4	3.1531	58.6308	1.1797	15.1647	82.2963	−63.5806	1712.0680
0.004	1714.0	3.1766	69.4408	1.1626	15.0253	78.1711	−72.7931	1699.0201
0.002	1708.0	3.1992	80.2521	1.1131	14.0239	33.3056	−85.3796	1593.0061
90% of DMF – Water								
0.010	1700.8	3.4323	48.1653	1.1123	16.9986	78.1003	−52.1302	1817.2362

Conc. (kg mol^{-1})	Us (ms^{-1})	βs x 10^{-10} (m^{2}N^{-1})	Lf (A^0)	RA	τ x 10^{-6} (s)	Φk x 10^{-3} (m^{2}N^{-1})	Φv (m^{3}mol^{-1})	Zs (kgm^{-2}s^{-1})
0.008	1692.6	3.4516	48.9123	1.1012	15.9785	74.0423	−58.1032	1730.2316
0.006	1645.6	3.5032	59.1362	1.0989	15.1213	73.1456	−64.0036	1700.1023
0.004	1636.9	3.5789	70.1645	1.0986	15.0210	69.2365	−73.1023	1656.3026
0.002	1613.6	3.6231	82.3162	1.0976	14.0023	30.1032	−86.1032	1585.1034

Table III: Velocity (Us), Adiabatic Compressibility (βs), Intermolecular Free Length (Lf), Relative Association (RA), Viscous Relaxation Time (τ), Apparent Molar Compressibility (Φ$_k$), Apparent Molar Volume (Φ$_v$) and Specific Acoustic Impedance (Zs) of W1 in Different Concentrations and Different Percentages of DMF–Water at 10 °C (283K).

Conc. (kg mol^{-1})	Us (ms^{-1})	βs x 10^{-10} (m^{2}N^{-1})	Lf (A^0)	RA	τ x 10^{-6} (s)	Φk x 10^{-3} (m^{2}N^{-1})	Φv (m^{3}mol^{-1})	Zs (kgm^{-2}s^{-1})
80% of DMF – Water								
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
85% of DMF – Water								
0.010	1492.9	4.9074	95.1003	1.0218	16.0087	52.9423	42.0665	1400.0024
0.008	1646.1	3.7704	92.1237	1.0408	16.0121	74.8982	82.5091	1656.1408
0.006	1711.4	3.4699	80.1528	1.0509	16.0217	101.9737	90.4679	1732.3813
0.004	1727.8	3.2311	69.1042	1.0984	16.2007	113.2814	102.7432	1844.1925
0.002	1733.6	3.1765	57.1493	1.1077	17.1673	425.6987	104.8672	1870.0735
90% of DMF – Water								
0.010	1482.6	4.5102	96.0321	1.0213	15.9878	46.0032	100.1034	1395.2148
0.008	1640.3	3.7906	93.1023	1.0398	15.9923	66.1456	100.0008	1645.1452
0.006	1700.1	3.5132	81.0090	1.0456	16.1023	99.2362	91.0456	1721.1456
0.004	1716.3	3.3316	70.3623	1.1012	16.4523	98.4862	79.2036	1826.9842
0.002	1725.9	3.2642	59.1236	1.1103	17.1009	400.1023	60.4631	1860.1346

Table IV: Velocity (Us), Adiabatic Compressibility (βs), Intermolecular Free Length (Lf), Relative Association (RA), Viscous Relaxation Time (τ), Apparent Molar Compressibility (Φ$_k$), Apparent Molar Volume (Φ$_v$) and Specific Acoustic Impedance (Zs) of W2 in Different Concentrations and Different Percentages of DMF–Water at 10 °C (283K).

Conc. (kg mol^{-1})	Us (ms^{-1})	βs x 10^{-10} (m^{2}N^{-1})	Lf (A^0)	RA	τ x 10^{-6} (s)	Φk x 10^{-3} (m^{2}N^{-1})	Φv (m^{3}mol^{-1})	Zs (kgm^{-2}s^{-1})
80% of DMF – Water								
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
85% of DMF – Water								

Conc. (kg mol^{-1})	Us (ms^{-1})	βs x 10^{-10} (m^{2}N^{-1})	Lf (A^0)	RA	τ x 10^{-6} (s)	Φk x 10^{-3} (m^{2}N^{-1})	Φv (m^{3}mol^{-1})	Zs (kgm^{-2}s^{-1})
0.010	1501.8	4.8883	96.8119	0.9976	16.8604	44.8490	32.5183	1493.8941
0.008	1625.6	4.0005	90.0716	1.0028	16.9511	46.6181	81.4018	1543.9912
0.006	1700.9	3.4492	81.4811	1.0547	17.1332	64.4971	95.4243	1722.1850
0.004	1717.3	3.3632	70.1022	1.0575	17.3170	91.8145	109.6340	1749.4420
0.002	1723.1	3.1677	52.8213	1.1073	18.6161	405.9811	111.1415	1851.1521
90% of DMF – Water								
0.010	1498.0	4.8905	97.0023	0.9879	15.9878	36.2315	100.1236	1489.2130
0.008	1630.6	4.1236	91.0632	1.0012	16.0056	37.8263	99.1456	1533.1406
0.006	1716.4	4.0863	83.1023	1.0449	17.1513	55.3215	96.1023	1720.4315
0.004	1729.3	4.0132	72.3126	1.0612	17.4526	82.1326	79.1456	1735.1479
0.002	1736.2	4.0013	55.1186	1.0836	18.0231	400.1023	61.3126	1800.2136

Ultrasonic velocities are incorporated in Table I to Table IV for different solutes. In case of M6 to M7, 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 as studied by J. H. So and others [12–14]. This suggests that disruption of water structure is enhanced further with the addition of solute. As we move towards pure solvent system, velocity values tend to decrease with the increase in DMF content in the mixture. Probably, this increase in concentration of DMF is allowing the sound wave to travel freely in solution and hence it decreases.

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. Because of this, the adiabatic compressibility decreases with the increase in concentration. Also, as the percentage of DMF increases in solvent system, the intestinal species of water get completely filled and more and more solvent molecules will be available to solute. It reflects increase in the value of adiabatic compressibility with increase in percentage composition of DMF in solvent system as Verma and Kumar mentions [15]. The data shows that Lf increases with increase in the DMF content. Hence ion–solvent interactions increase. As ion–solvent interaction

increases, it leads to smaller electrical conductivity. The similar findings are of earlier authors [16].

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 which has been studied by Abida [17]. In present study, the relative association is maximum in 90 % DMF–water.

Apparent Molar Compressibility (Φ_k) represents the magnitude of solute–solvent interaction occurring in the systems. (Φ_k) decreses with increase in percentage of organic solvent, this indicates that the organic solvent become more compressible in the lower percentage of solvent–water mixture. Hence interactions are more on addition of water as Aswar and others have observed[18].

The apparent molar volume Φ_v is defined as the change in volume of the solution for the added one mole of a particular component at constant temperature and pressure without any appreciable change in the concentration. It is a thermodynamic property which helps in explaining solvation behaviour of electrolyte in solution. Φ_v was calculated from the density of the solution and solvent.

In the systems M6 and M7, Φ_v are negative and with increase in percentage of DMF in solvent systems, Φ_v decreses. This indicates that the organic solvent becomes more compressible in the lower percentage of solvent–water mixture. Interactions are more on addition of water resulting in more association between solute and solvents according to Sumathi [19].

Zs is found to increase with increase in concentration of solute. As anticipated Zs appears almost reciprocal of adiabatic compressibility.

At lower percentage of solvent, presence of bulkier/solvated ion due to ion–solvent solvent–solvent interaction which restricts the free flow of sound waves, both density and velocity decreases as DMF content increases. Hence acoustic impedance also decreases. Similar decrease has been reported Syal and Baluja [20–21] in case of PVP and PVA in DMSO+H_2O solvent system. This is a clear indication of enhanced solute–solvent interactions.

5. Acknowledgements

6. References

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