



Molecular Interactions of Substituted Thiosemicarbazides and Thioxadizenes in dimethylformamide and dimethylsulphoxide

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ABSTRACT

The experimental data of ultrasonic velocity, density, viscosity have been obtained for some thiosemicarbazides and thioxadizenes in 85% DMSO over the concentration range of, (0.002 to 0.01) mol.Kg⁻¹. The derived parameters such as adiabatic compressibility (β_s), apparent molar volume of solute (Φ_v), limiting apparent molar volume of solute (Φ_v^0), 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, (β_s), Apparent Molar Compressibility (Φ_k), Apparent Molar Volume (Φ_v), limiting apparent molar volume (Φ_v^0)

INTRODUCTION

In the recent years, measurements of the Ultrasonic velocity are helpful to interpreted solute-solvent, ion solvent interaction in aqueous and non-aqueous medium¹⁻⁴. Jahagirdar⁵ 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. Meshram⁶ et. al. studies the different acoustical properties of some substituted Pyrazolines in binary mixture acetone-water and observed variation of ultrasonic velocity with concentration. Palani⁷ 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. Voleisines⁸ have studied the structural properties of solution of lanthanide salt by measuring ultrasonic velocity..Tadkalkar⁹ et. al. have studied the acoustical and thermodynamic properties of citric acid in water at different temperature. Mishra¹⁰ 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 workers¹¹. 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 (± 0.01 s). 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 thioxadiazine	
W2	3-[pyrid-4yl]-5H-6- o-tolylimino-1, 2, 4, 5 thioxadiazine	



W3	3-[pyrid-4yl]-5H-6-p-chloro phenyl thioxadiazine imino-1,2,4,5	
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EXPERIMENTAL AND COMPUTED DATA

Table I: Values of Velocity (U_s), Viscosity (η_s), Adiabatic Compressibility (β_s), Apparent Molar Compressibility (Φ_k) and Apparent Molar Volume (Φ_v) for all solutes in 85% DMSO-Water system at 283K.

Conc. (kg mol ⁻¹)	U_s (ms ⁻¹)	η_s x10 ³ (Nsm ⁻²)	β_s x10 ⁻¹⁰ (m ² N ⁻¹)	Φ_k x10 ⁻³ (m ² N ⁻¹)	Φ_v (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_k^0), slope (S_k), limiting molar volume (Φ_v^0), slope (S_v) for different solutes in 85% DMSO-Water system at 283 K.

Solutes	A $(\text{dm}^3\text{mol}^{-1})^{1/2}$	B $(\text{dm}^3\text{mol}^{-1})$	$\Phi_k^0 \times 10^{-3}$ $(\text{m}^2\text{N}^{-1})$	$S_k \times 10^{-3}$ $(\text{N}^{-1}\text{m}^{-1}\text{mol}^{-1})$	Φ_v^0 $(\text{m}^3\text{mol}^{-1})$	S_v $(\text{m}^3\text{kg}^{-1/2}\text{mol}^{-3/2})$
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 interactions¹³⁻¹⁴. 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 findings¹⁵. 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 equation¹⁵. $\eta / \eta_0 = 1 + AC^{1/2} + BC$

which can be written as $[\eta / \eta_0 - 1] / \sqrt{C} = A + BC^{1/2}$

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 $[\eta / \eta_0 - 1] / \sqrt{C}$ 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 torsional force¹⁶⁻¹⁷. 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 forces¹⁸⁻²⁰ 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 (β_s): 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 authors²¹⁻²². As concentration increases, a larger portion of the water molecules are electrostricted and the amount of bulk





water decreases causing the compressibility to decrease. Decrease in adiabatic compressibility 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 Compressibility (Φ_k): Apparent molar compressibility Φ_k , was calculated by using the following equation ²⁴⁻²⁵:

$$\Phi_k = [(1000 (d\beta_s - ds \beta_0) / C d\beta_s) + [\beta_s M / ds].$$

The calculated values are shown in Table-I. In the above equation, all the terms are constant, except concentration C and compressibility β_s . Hence, Gucker²⁶ suggested the equation, $\Phi_k = \Phi_k^0 + S_k C^{1/2}$ on the basis of Debye-Huckel theory. The limiting molar compressibility Φ_k^0 and the slope S_k are shown in Table-II. S_k and Φ_k^0 represent the measure of solute-solute and solute-solvent interactions²⁷ respectively.

The comparative high values of Φ_k^0 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 reflected from the lower values of S_k . However, for W1, W2 and W3 lower values of Φ_k^0 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 concentration²⁸⁻²⁹. This was calculated using the following equation:

$$\Phi_v = (M / ds) + [1000 [(d\sigma - ds) / C ds d\sigma]$$

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 $\Phi_v = \Phi_v^0 + S_v C^{1/2}$, proposed by Masson³⁰. Φ_v^0 gives the information about solute-solvent interactions. Table-II reveals for the solutes M3, M5 and M7, Φ_v^0 values are positive and large, indicating the presence of strong solute-solvent interactions. But for W1, W2 and W3, Φ_v^0 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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