ULTRASONIC STUDIES OF ORGANOMERCURY DITHIO COMPLEXES IN ACETONE AT VARIOUS TEMPERATURES

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ABSTRACT

Ultrasonic velocity and density measurements of various solutions of different concentrations of O, O' - Propylene dithio phosphate of mercury [phHgS(S)POGO]G=-CH2C(H)-CH3 in acetone have been carried out at 30, 35, 40° C . The experimental data were used to calculate other thermodynamic and acoustic parameters such as Isentropic compressibility, intermolecular free length, molar sound velocity, molar volume, apparent molar compressibility, specific acoustic impedance and salvation number. The significant information about intermolecular interactions between an organometallic moiety and acetone (non aqueous) have been obtained.

I. INTRODUCTION

Ultrasonic velocity and its related properties have been extensively used to study physiochemical behaviour and molecular interactions in a variety of solution containing organic and inorganic molecules[1-5] however , little attention has been paid to organometallic solutes [6-7]which have attained considerable importance in recent years . In continuation to our earlier work on ph2SnCl2 in acetone and acetonitrile, Me2TeI2 in acetone system[8-10], the present study was undertaken to examine the intermolecular interaction of organomercury dithio complexes in acetone at various temperatures. Three organomercury dithio complexes were synthesized[11] and their reactivity with various soft Lewis acids and Lewis bases was reported[12-13]. The organomercury compounds are extensively used in biological fields as fungicides, insecticides and bactericides and in the industrial field as stabilisers, oil antioxidant and water repellent etc. Hg-C bonding in organomercury compounds is relatively weak. These compounds are insoluble in water, sufficiently stable and having no sharp melting point. These compounds show dissociation reaction in benzene when kept for at least 12 hours in solvent at room temprature. The final product of dissociation reaction is mercury.

2. EXPERIMENTAL

The experimental technique and instrumentation are similar to those reported earlier[8-10]. The ultrasonic velocity was measured by using a multi frequency interferometer working at 1MHz. The accuracy of the ultrasonic values was ± 0.2%. O ,O- Propylene dithio phosphate of mercury was synthesized[11]. The solution of different concentrations were prepared in acetone and kept for two hours in a thermostat at the desired temperature. Organomercury compounds are partially soluble in solvent. The densities of solvent and solutions at different temperatures were measured with a pyknometer and accuracy of the results was ± 0.1 gm/cm³. Various acoustic parameters such as adiabatic(isentropic) compressibility β, intermolecular free length Lf , specific acoustic impedance Z, molar volume V, molar sound velocity R, apparent molar compressibility ØK and salvation number Sn have been calculated as mentioned earlier[8-10].

3. RESULT AND DISCUSSION

From the measured ultrasonic velocity and density measurements, various parameters V, , Lf , Z , R, $\emptyset K$ and Sn are calculated for O ,O- Propylene dithio phosphate of mercury- acetone system and results are presented graphically in Fig. 1-5 with data table 1-5.

The primary effect of dissolution of a solute in a solvent is a change in the compressibility of the solution because of various types of interactions[14] taking place between solute and solvent molecules. A higher interaction brings the interacting molecules closer , thus reducing the intermolecular free length and consequently making the solution harder to compress due to decrease of isentropic compressibility. Since the bonding in organomercury complex is predominantly covalent the compressibility is not that low as in the case of electrolyte where it can reach thousands of atmospheres. The ultrasonic velocity (V) of for O, O- Propylene dithio phosphate of mercury in acetone gradually decreases with rise in temperature. The behavior is due to corresponding changes in isentropic compressibility and density. The intermolecular free length (Lf) decreases linearly with the increasing molar concentration over the entire range of concentration under investigation. The decrease of Lf in the system is due to a closer approach of the interacting molecules as O ,O- Propylene dithio phosphate of mercury molecule is having large surface area which results in the decrease of compressibility also. The change in Lf, according to Eyring and Kincaid[15] also indicate that there is significant interaction between solute and solvent molecules. The molar volume, molar sound velocity, specific acoustic impedance and apparent molar compressibility increase with increasing concentration.

The ultrasonic velocity, density and specific acoustic impedance decrease with increasing temperature while isentropic compressibility, intermolecular free length, molar volume increase with the increasing temperature. The increase of isentropic compressibility and intermolecular free length is due to increase in the average kinetic energy of the interacting molecules as reported by Mednis[16].Although molar sound velocity increases with concentration. It is independent of temperature.

It is concluded from the present investigation that significant interaction takes place in the binary system of O, O- Propylene dithio phosphate of mercury in acetone which increases with concentration. The interaction increases linearly. The interaction is found to decrease with the increase of temperature as non aqueous solvent gets vaporized on increasing temperature.

The above results indicate that the solutions in which solute are partially soluble can show considerable interactions in solution.

Table:-1 Conc. of solutions and their respective ultrasonic velocities (m/s)

conc.(moles/L)	Velocity at 30°C	Velocity at 35°C	Velocity at 40°C
0	1117	1100	1091.32
0.2384	1124	1114.6	1101
0.2981	1131	1120.3	1109.4
0.3726	1134	1125	1118.2
0.4657	1140	1132.1	1124.7
0.5118	1149	1137	1130.5
0.5445	1152	1142	1133.1
0.7127	1156	1145	1138

SERIES 1 at 30°C
SERIES 2 at 35°C
SERIES 3 at 40°C
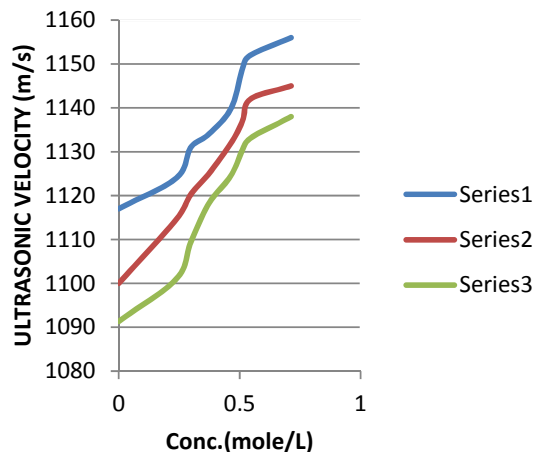
FIG.1

Table:- 2 Concentration of solutions and their respective isentropic compressibility)(cm²dyne⁻¹)

Conc.(mole/l)	β x10⁻¹² at 30°C	β x10⁻¹² at 35°C	β x10⁻¹² at 40°C
0	103.71	106.98	101.38
0.2384	92.12	94.47	97.21
0.2981	90.07	92.51	94.57

0.3726	89.16	90.83	92.97
0.4657	87.81	89.67	90.96
0.5118	85.66	87.84	89.31
0.5445	83.98	85.94	87.5
0.7127	77.71	81.05	83.71

SERIES 1 at 30°C
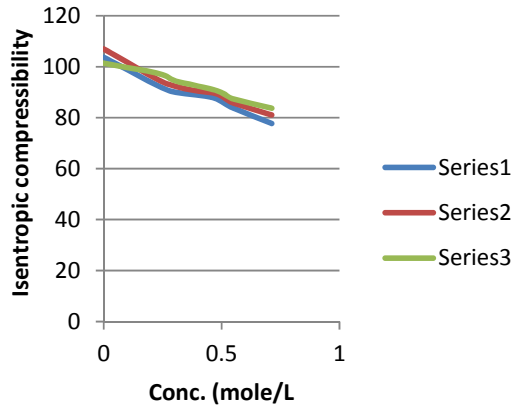**SERIES 2 at 35°C**
SERIES 3 at 40°C

FIG.2

Table:- 3   Conc. of solutions and their respective inter molecular free length values (Lf)

conc.(moles/L)	Lf(A°) at 30°C	Lf(A°) at 35°C	Lf(A°) at 40°C
0	0.6423	0.6581	0.6708
0.2384	0.6055	0.6186	0.632
0.2981	0.5988	0.6121	0.624
0.3726	0.5957	0.6065	0.619
0.4657	0.5912	0.6027	0.612
0.5118	0.5839	0.5965	0.606
0.5545	0.5782	0.59	0.6
0.7127	0.5562	0.5729	0.587

SERIES 1 at 30°C
SERIES 2 at 35°C
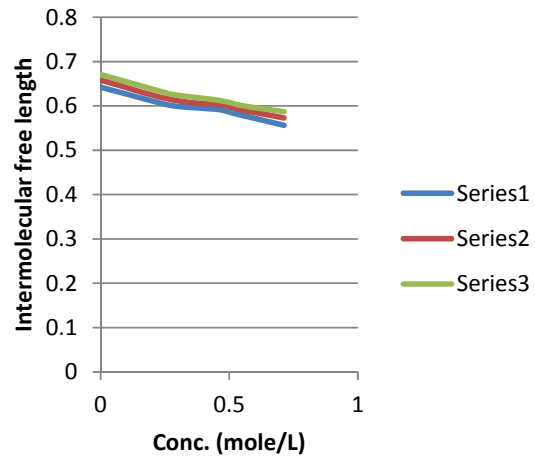**SERIES 3 at 40°C**

FIG.3

Table:- 4   Conc. of solutions and their respective specific acoustic Impedance(Z x 10^{-5})

conc.(moles/L)	Z at 30°C	Z at 35°C	Z at 40°C
0	0.868	0.849	0.837
0.2384	0.965	0.949	0.934
0.2981	0.981	0.964	0.953
0.3726	0.988	0.978	0.961
0.4657	0.998	0.985	0.977
0.5118	1.015	1.001	0.99
0.5545	1.033	1.018	1.008
0.7127	1.113	1.077	1.049

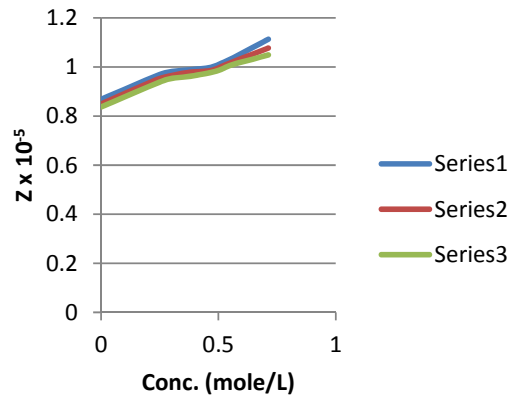**SERIES 1 at 30°C**
SERIES 2 at 35°C
SERIES 3 at 40°C

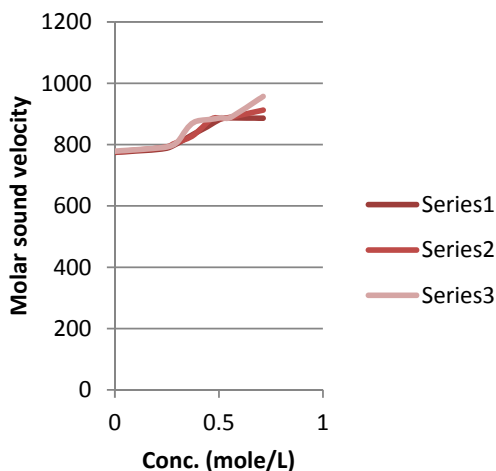**FIG. 4**

Table:- 5 Conc. of solutions and their respective Molar sound velocity (R)

conc.(moles/L)	R at 30°C	R at 35°C	R at 40°C
0	774.53	775.85	778.54
0.2384	786.93	791.19	791.23
0.2981	803.65	807.66	807.3
0.3726	831.93	828.36	870.25
0.4657	867.25	884.24	882.73
0.5118	884.81	885.08	887.86
0.5545	887.13	888.98	888.51
0.7127	886.09	912.73	957.13

SERIES 1 at 30°C
SERIES 2 at 35°C
SERIES 3 at 40°C

FIG. 5

4.References:

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