

Ultrasonic Studies of $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in Dioxane + Water Solvent at 303.15 K

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Abstract: Various acoustic parameters such as isentropic compressibility (β_s), intermolecular free length (L_f), apparent molar volume (Φ_v), apparent molar compressibility (Φ_k), molar compressibility (W), molar sound velocity (R), acoustic impedance (Z) of $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 10%, 20% and 30% Dioxane + Water at 303.15K have been determined from ultrasonic velocity (U), density (ρ) and relative viscosity (η_r) of the solution. These parameters are related with the molar concentration of the solution and reflects the distortion of the structure of the solvent i.e. Dioxane + Water.

Keywords: Ultrasonic velocity, acoustic parameter, density, relative viscosity, Dioxane + water.

1. INTRODUCTION

The ultrasonic studies find extensive applications as sound speed in liquids and liquid mixtures is intrinsically related with many parameters which characterize the physico chemical behaviour of the liquids and liquid systems. Mixed solvents rather than single pure liquids are of utmost practical importance in most of the chemical and industrial processes as they provide a wide range mixture of two or more components in varying proportions so as to permit continuous adjustment of the derived properties of the medium. Intermolecular interactions in various binary liquid mixtures at different temperatures have been studied by several authors (Bhoj *et al.* 2006, Nain *et al.* 2008, Thanuja *et al.* 2011, Zareena *et al.* 2013) Physico chemical properties like density, viscosity and speed of sound have got considerable importance in forming theoretical models as well as their applications in a number of branches of science. A considerable progress has been made theoretical understanding of liquid – liquid mixture (Anil *et al.* 2007, Shahla *et al.* 2009, Rajgopal *et al.* 2011). An attempt has been made to elucidate the ion-ion interaction between nitroprusside ions and ion-solvent interaction of sodium nitroprusside in aquo-organic mixtures at 308.15 K (Smrutiprava *et al.* 2013). The binary mixture are indispensable for many chemical process industries e.g. petroleum, petrochemicals, where physico chemical processes are involved to handle the mixtures of hydrocarbons, alcohols, ketones etc. for accurate designing equipment it is necessary to know the interaction between the components of mixture. The thermodynamic studies of binary solutions have attracted much attention of scientists and experimental data on a number of systems are available from review and publications. Viscosity, density measurements and the properties derived from these are excellent tools to detect solute – solute and solvent interactions. It is used in different fields of scientific researches in physics, chemistry, biology, medicines and industries. The present work deals with the measurement of density (ρ), relative viscosity (η_r), apparent molar volume (Φ_v), ultrasonic velocity (U) and the derived acoustical parameters with Dioxane + Water mixture at 303.15 K using $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ as electrolyte.

2. MATERIALS AND METHOD

The solute Cadmium nitrate, $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (E-Merck) used is of high purity and found up to the standard. The solvents used were purified by appropriate method. Dioxane (E-Merck) and water were triple distilled. Purity was about 99.9% which was in good agreement with the standard values of density, viscosity etc. the solvents of different Dioxane contents were prepared by taking required volume of Dioxane in distilled water. The densities of pure components and binary mixtures were measured using pre-calibrated pycnometer with an accuracy of 0.053% at

303.15 K. Viscosities of pure liquids and their mixtures were measured using Ostwald's Viscometer. The flow time of pure liquids and liquid mixtures were measured using an accurate stop watch with a precision of ± 0.15 . Ultrasonic velocity was measured by using single crystal Ultrasonic interferometer (Mittal Enterprise, Model F-81) operating at a frequency of 5 MHz. Water from a thermostatically regulated bath (Toshniwal, India) equipped with Jumo D.B.P. temperature sensor was circulated with a sample holder (with double wall) to maintain the temperature of the liquid constant at 303.15 K with a precision of 0.01 K.

3. RESULTS AND DISCUSSION

The apparent molar volume (Φ) was determined from the following:

$$\phi = \frac{M}{\rho_0} - \frac{[\rho_0 - \rho_0]}{\rho_0} \times \frac{1000}{C}$$

and the results are noted in (Table 1) where:

M = molecular mass of the solute

ρ_0 = Density of the solvent

ρ = density of the solution

C = Molar concentration of the solution. The data obtained follow Masson's equation (Masson 1929) ($\phi = \phi_0 + s_v \sqrt{C}$) (Plot of ϕ vs. \sqrt{C} is linear).

The values of limiting apparent molar volume (ϕ_0) and slope (s_v) calculated from the graph are recorded in Table 2. The positive value of S_v indicates ion – ion interaction. The increase of Φ_0 with increasing concentration of Dioxane may be attributed due to low charge density.

The relative viscosity (η_r) values are determined from the following equation and recorded in (Table 1)

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0} \times \frac{\rho}{\rho_0}$$

Where η_r is relative viscosity and η , ρ and t , η_0 , ρ_0 and t_0 are the coefficient of viscosity, density and time of efflux of the solution and solvent respectively. The values so obtained show that the relative viscosity (η_r) increases with the increase in concentration of Dioxane. This may be due to increase in the degree of hydrogen bonding between Dioxane and water. The relative viscosity increases with increase in concentration of the solute. This is in agreement with the work of Widemann et al. 1981

The plot of $\left(\frac{\eta_r - 1}{\sqrt{C}} \right)$ vs. \sqrt{C} is linear (Fig.1), which is in good agreement with the Jones –

Dole equation (Jones et al. 1929)

$$\eta_r = 1 + A\sqrt{C} + BC$$

Table1. Variations of η_r , ρ and ϕ at different concentrations of $Cd(NO_3)_2$ in Dioxane + Water at 303.15 K.

Concentration in mol dm ⁻³	η_r ($\eta_r \times 10^3$) in Kg m ⁻¹ s ⁻¹	ρ in g ml ⁻¹	ϕ in cm ³ mol ⁻¹
10% Dioxane + Water			
0.1000	1.07995	0.9987	102.7187
0.0750	1.06122	0.9952	102.4349
0.0500	1.04222	0.9917	102.0982
0.0250	1.02270	0.9882	101.6594
0.0100	1.01034	0.9861	101.2700
0.0075	1.00815	0.9857	101.1802
0.0050	1.00588	0.9853	101.0738
0.0025	1.00344	0.9849	100.9350

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0.0010	1.00178	0.9847	100.8119
20% Dioxane + Water			
0.1000	1.08630	0.9877	107.9251
0.0750	1.06601	0.9844	107.6403
0.0500	1.04545	0.9809	107.3026
0.0250	1.02435	0.9775	106.8625
0.0100	1.01103	0.9754	106.4720
0.0075	1.00868	0.9750	106.3820
0.0050	1.00624	0.9747	106.2752
0.0025	1.00364	0.9743	106.1360
0.0010	1.00186	0.9740	106.0125
30% Dioxane + Water			
0.1000	1.10078	0.9713	112.6472
0.0750	1.07691	0.9688	112.3595
0.0500	1.05275	0.9654	112.0183
0.0250	1.02804	0.9620	111.5736
0.0100	1.01254	0.9599	111.1790
0.0075	1.00982	0.9595	111.0880
0.0050	1.00702	0.9592	110.9801
0.0025	1.00404	0.9588	110.8395
0.0010	1.00203	0.9586	110.7147

Table2. Limiting apparent molar volume (Φ_0), Limiting Slope (S_v), A and B of Cd(NO₃)₂ in Dioxane + Water at 303.15 K.

Parameter	10%	20%	30%
Φ_0 (cm ³ mol ⁻¹)	100.6	105.8	110.5
S_v (cm ^{9/2} mol ^{-3/2})	6.70	6.72	6.79
$A \times 10^2$ (mol ^{-1/2} L ^{1/2})	3.43	3.51	3.60
B (mol ⁻¹ L)	0.691	0.752	0.894

The increasing value of A with Dioxane content supports the increase in electrostatic attraction as well as ion- solvent interactions while the increase in S_v value attribute to large size of solvent molecules and strong association between water and organic solvent through hydrogen bonding.

The ultrasonic velocity (U) (Rajendran et al. 1996, Haribabu et al. 1996), isentropic compressibility (β_s) (Jacobson et al. 1985), molar compressibility (W), molar sound velocity (R), acoustic impedance (Z) (Nikam et al. 1990), intermolecular free length (L_f) and apparent molar compressibility (Φ_k) of Cd(NO₃)₂·2H₂O in 10%, 20% and 30% Dioxane + water at 303.15 K are recorded in (Table 3) and (Fig. 2 – 7).

Table3. Variation acoustic parameters of Cd(NO₃)₂ in Dioxane + Water at 303.15 K.

Conc ⁿ . in mol dm ⁻³	U m sec ⁻¹	$\beta_s \times 10^{-11}$ cm ² dyne ⁻¹	W	R	$Z \times 10^{-5}$ in cm ² dyne ⁻¹	$L_f \times 10^{-11}$	$\Phi_k \times 10^{-14}$ in cm ² dyne ⁻¹
10% Dioxane+ Water							
0.1000	1567.6	4.0747	5.2291	128.4574	15.6556	4.0299	-1.5549
0.0750	1566.4	4.0953	5.2437	128.8763	15.5888	4.0401	-1.7935
0.0500	1565.0	4.1171	5.2583	129.2926	15.5201	4.0508	-2.2480
0.0250	1563.8	4.1380	5.2731	129.7174	15.4535	4.0611	-3.5995
0.0100	1562.0	4.1564	5.2809	129.9437	15.4029	4.0701	-5.0776
0.0075	1561.0	4.1634	5.2818	129.9687	15.3868	4.0735	-5.8144
0.0050	1560.0	4.1704	5.2827	129.9937	15.3707	4.0770	-7.4567
0.0025	1558.0	4.1829	5.2826	129.9909	15.3447	4.0830	-12.0318
0.0010	1556.5	4.1918	5.2821	129.9755	15.3269	4.0874	-11.6959
0.0000	1555.0	4.2003	5.2811	129.9470	15.3105	4.0915
20% Dioxane+ Water							
0.1000	1600.0	3.9549	5.3100	130.7768	15.8032	3.9702	-1.9518
0.0750	1597.5	3.9806	5.3228	131.1465	15.7258	3.9831	-2.0788
0.0500	1595.5	4.0047	5.3370	131.5552	15.6508	3.9951	-2.2011
0.0250	1593.0	4.0316	5.3509	131.9548	15.5708	4.0085	-2.7345
0.0100	1591.5	4.0478	5.3593	132.1971	15.5228	4.0166	-6.2305
0.0075	1591.0	4.0518	5.3605	132.2309	15.5123	4.0186	-4.7036
0.0050	1590.0	4.0582	5.3610	132.2444	15.4977	4.0217	-4.6563
0.0025	1588.0	4.0701	5.3609	132.2432	15.4719	4.0276	-4.8309
0.0010	1586.0	4.0816	5.3604	132.2284	15.4476	4.0333	-5.8640
0.0000	1585.0	4.0872	5.3599	132.2141	15.4363	4.0361

30% Dioxane+ Water							
0.1000	1612.5	3.9596	5.3987	133.3304	15.6622	3.9726	-3.2149
0.0750	1610.5	3.9796	5.4087	133.6191	15.6025	3.9826	-3.9833
0.0500	1608.5	4.0036	5.4231	134.0342	15.5285	3.9946	-3.6979
0.0250	1606.5	4.0278	5.4376	134.4521	15.4545	4.0066	-6.9111
0.0100	1605.0	4.0441	5.4463	134.7043	15.4064	4.0148	-11.5126
0.0075	1604.0	4.0509	5.4473	134.7325	15.3904	4.0181	-6.1522
0.0050	1601.5	4.0648	5.4464	134.7046	15.3616	4.0250	-5.8791
0.0025	1598.0	4.0843	5.4449	134.6625	15.3216	4.0347	-5.3723
0.0010	1597.0	4.0903	5.4449	134.6625	15.3088	4.0376	-7.3838
0.0000	1596.0	4.0958	5.4444	134.6485	15.2977	4.0403

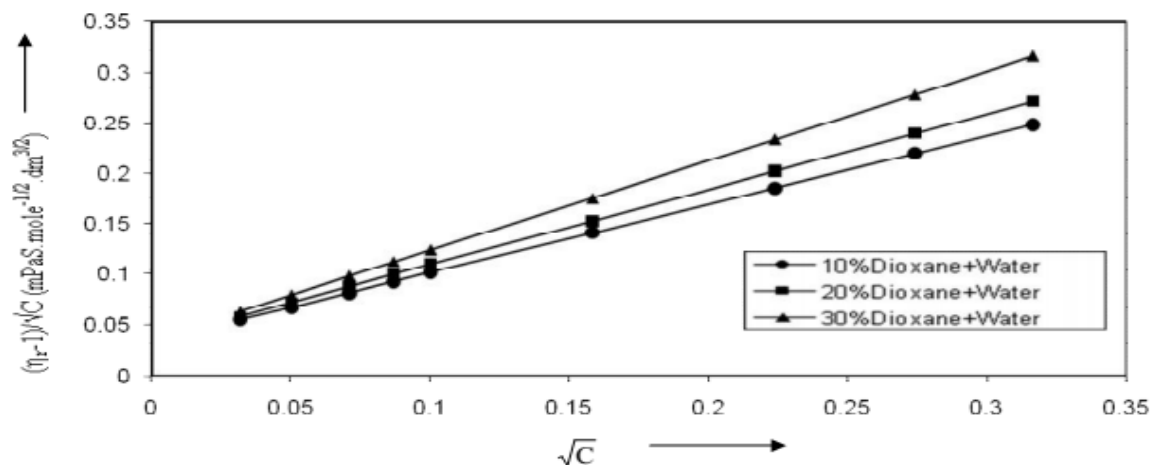


Fig1. Viscosity of $Cd(NO_3)_2$ in Dioxane + Water at 303.15 K.

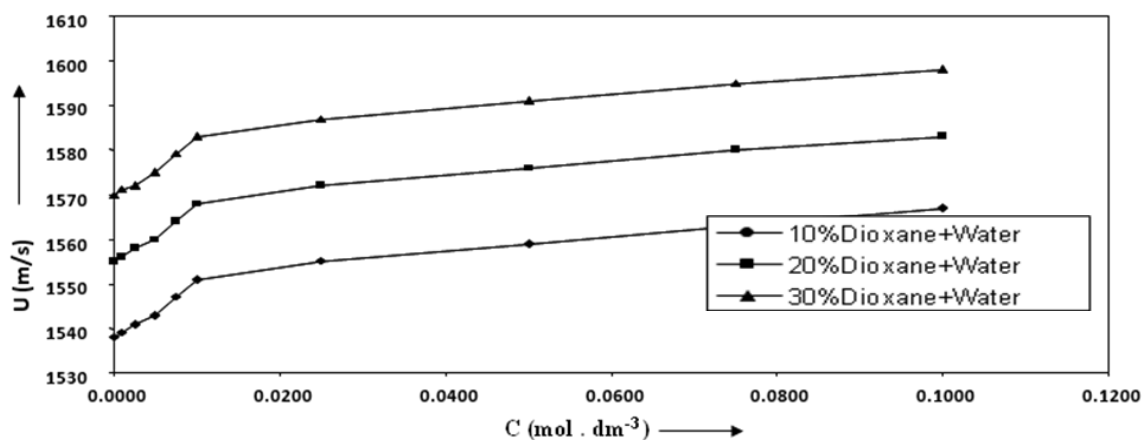


Fig2. Ultrasonic velocity of $Cd(NO_3)_2$ in Dioxane + Water at 303.15 K.

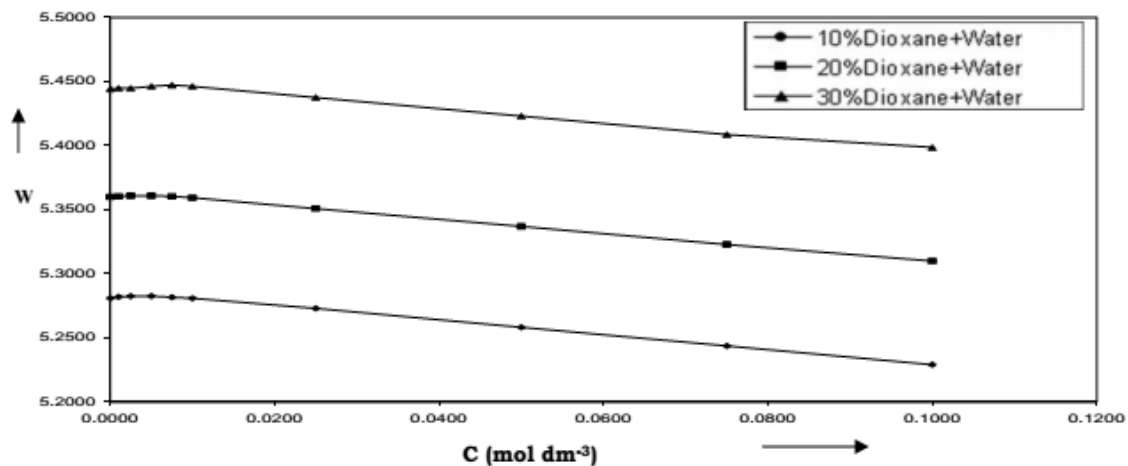


Fig3. Molar Compressibility (W) of $Cd(NO_3)_2$ in Dioxane + Water at 303.15 K.

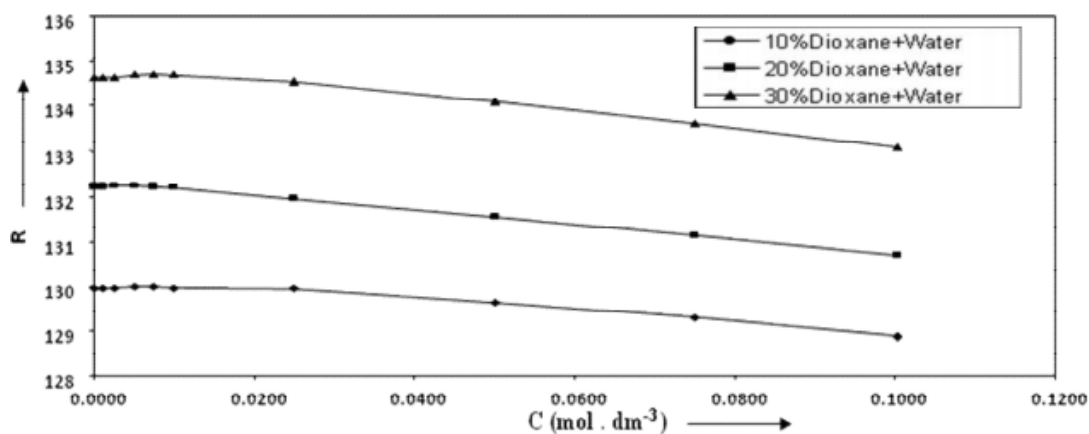


Fig4. Molar Sound velocity (R) of $\text{Cd}(\text{NO}_3)_2$ in Dioxane + Water at 303.15 K.

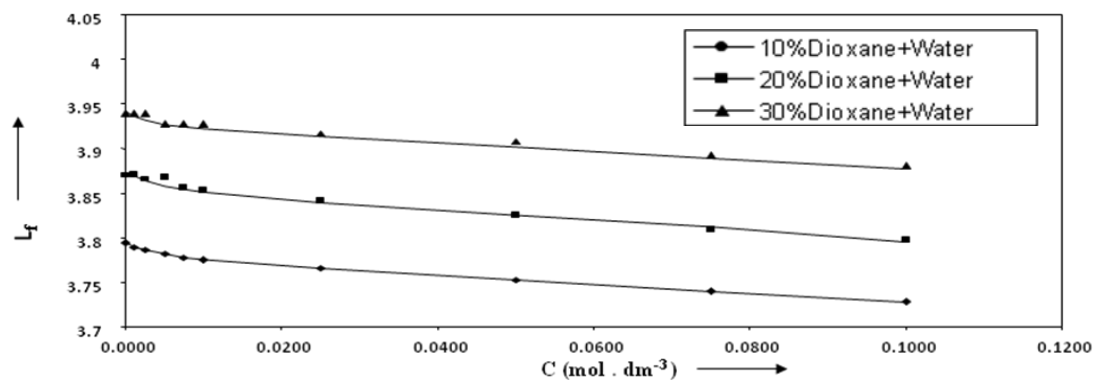


Fig5. Intermolecular Free Length (L_f) of $\text{Cd}(\text{NO}_3)_2$ in Dioxane + Water at 303.15 K.

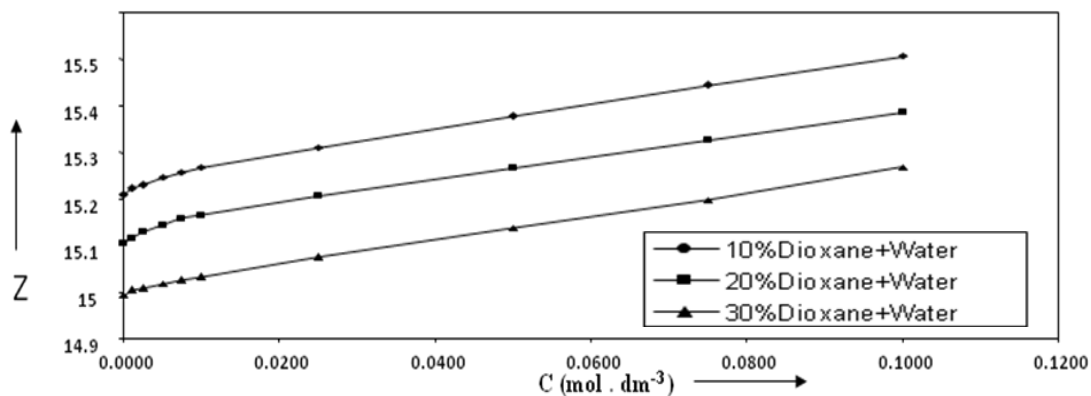


Fig6. Acoustic Impedance (Z) of $\text{Cd}(\text{NO}_3)_2$ in Dioxane + Water at 303.15 K

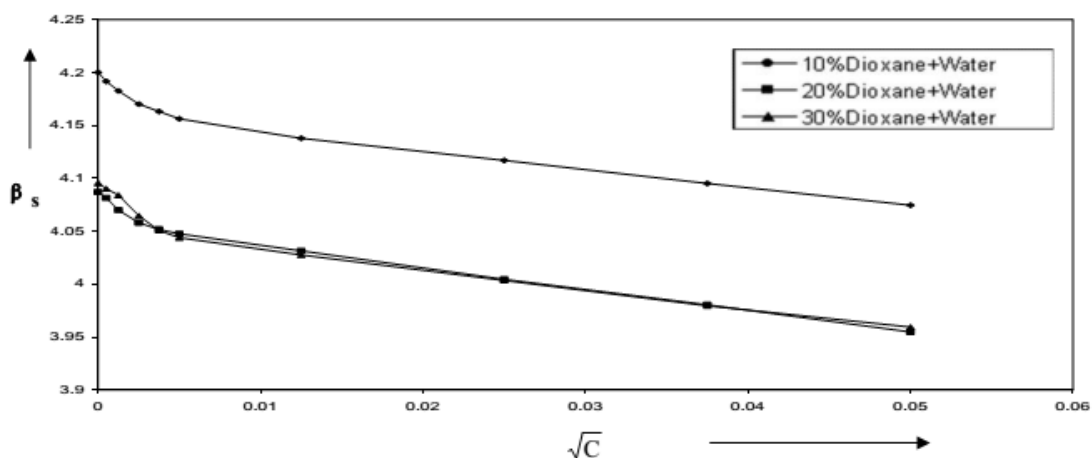


Fig7. β_s vs. of $\text{Cd}(\text{NO}_3)_2$ in Dioxane + Water at 303.15 K

4. CONCLUSIONS

The data measured shows that the ultrasonic velocity increases with increase in concentration in all cases along with molar compressibility (W), molar sound velocity (R) while intermolecular free length (L_f) and acoustic impedance (Z) decreases with increase in concentration. The increase in isentropic compressibility (β_s) with decreasing concentration suggest minimum interaction between the unlike molecules (i.e. solute & solvent molecules). Acoustic impedance (Z) decreases with decrease in concentration, which supports the possibility of weak interactions between unlike molecules and is also used for accessing the absorption of sound in a media. The increasing ultrasonic velocity (U) and molar compressibility (W) with increasing concentration represents the decrease in cohesive force which is responsible for the structure breaking nature of the solute. The hydrogen bond existing Dioxane and water is disrupted by the solute molecules and thereby formation of new bonding between solute and solvent molecules has occurred. As most of the solvent molecules are engaged in interaction with the solute, addition of more solute molecules to the solvent leads to the acceleration of the process of breaking of aggregates of solvent molecules. This process leads to the inhibition of propagation of sound waves due to large sized solute molecules acting as structure promoters. To conclude the formation of more cluster of the solute – solvent molecules with increase in hydro-dynamic volume increases the isothermal compressibility.

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