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Research Paper

Ultrasonic studies of $Ni(NO_3)_2.6H_2O$ in glycol + 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 $Ni(NO_3).6H_2O$ in 10%, 20% and 30% Glycol + 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 reflect the distortion of the structure of the solvent i.e. Glycol + Water.

Keywords*: Ultrasonic Velocity, Acoustic Parameter, Density, Relative Viscosity, Glycol + 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 behavior 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 (Nain et al. 2008, Bhoj et al. 2006, Zareena et al. 2013, Thanuja et al. 2011) 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 (Rajgopal et al. 2010, Anil Kumar Nain et al. 2007, Shahla et al. 2009, and Rajgopal et al. 2011). 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 Glycol + Water mixture at 303.15 K using $Ni(NO_3).6H_2O$ as electrolyte.

2. Method and material

The solvents used were purified by appropriate method. Glycol (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 Glycol contents were prepared by taking required volume of glycol 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:

$$\varphi = \frac{M}{\rho 0} - \frac{(\rho - \rho 0)}{\rho 0} \times \frac{1000}{C}$$

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) $\left(\varphi = \varphi_0 + S_v\sqrt{C}\right)$

(Plot of φ vs. $\sqrt{C}$ is linear).

The values of limiting apparent molar volume $\left(\varphi_0\right)$ and slope $\left(S_v\right)$ 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 glycol may be attributed due to low charge density.

The relative viscosity $\left(\eta_r\right)$ 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 glycol. This may be due to increase in the degree of hydrogen bonding between glycol 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 (Jone et al. 1929)

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

The values of A and B obtained from the graph are recorded in "Table 2"

Table 1: Variations of η_r, ρ And φ at Different Concentrations:

Concentration in mol dm^{-3}	η_r	ρ in g ml^{-1}	φ in cm^{3}mol^{-1}
10% Glycol + Water			
0.1000	1.07239	1.019060	96.8286
0.0750	1.05546	1.017633	96.6104
0.0500	1.03828	1.016200	96.3516
0.0250	1.02062	1.014776	96.0143
0.0100	1.00942	1.013912	95.7150
0.0075	1.00744	1.013771	95.6460
0.0050	1.00537	1.013618	95.5642
0.0025	1.00315	1.013481	95.4575
0.0010	1.00163	1.013391	95.3629
20% Glycol + Water			
0.1000	1.08014	1.033281	103.0697
0.0750	1.06131	1.031852	102.8460
0.0500	1.04221	1.030421	102.5806
0.0250	1.02262	1.028989	102.2348
0.0100	1.01025	1.028126	101.9280
0.0075	1.00807	1.027934	101.8573
0.0050	1.00580	1.027840	101.7734
0.0025	1.00338	1.027695	101.6640
0.0010	1.00173	1.027609	101.5670
30% Glycol + Water			
0.1000	1.09860	1.046397	106.9823
0.0750	1.07612	1.044942	106.7569
0.0500	1.05212	1.043475	106.4896
0.0250	1.02761	1.042028	106.1412
0.0100	1.01227	1.041150	105.8320
0.0075	1.00959	1.041004	105.7607
0.0050	1.00683	1.040859	105.6762
0.0025	1.00390	1.040711	105.5660
0.0010	1.00195	1.040623	105.4682

Table 2: Limiting Apparent Molar Volume (Φ_0), Limiting Slope (Sv), A and B of Ni $(NO_3)_2$ in Glycol + Water at 303.15 K.

Parameter	10%	20%	30%
Φ_0 (cm^{3}mol^{-1})	95.2	101.4	105.3
S_v (cm$^{9/2}$mol$^{-3/2}$)	5.15	5.28	5.32
A×10^2 (mol$^{-1/2}$L$^{1/2}$)	3.19	3.27	3.34
B (mol^{-1}L)	0.623	0.698	0.893

The increasing value of A with glycol 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 $Ni(NO_3)_2.6H_2O$ in 10%, 20% and 30% glycol + water at 303.15 K are recorded in "Table 3" and "Fig.: 2 – 7".

4. Conclusion

The data measured shows that the ultrasonic velocity increases with increase in concentration (Fig. 2) in all cases along with molar compressibility (W) (Fig. 3), molar sound velocity (R) (Fig. 4) while intermolecular free length (L_f) (Fig. 5) and acoustic impedance (Z) (Fig. 6) decreases with increase in concentration. The increase in isentropic compressibility (β_s) (Fig. 7) 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 glycol 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. Recently similar study was reported (Das *et al.* 2013, Das *et al.* 2014) $^{\text{from}}$ our laboratory about the ion – solvent interaction of Drug and metal complex in mixed solvents.

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Table 3: Variation Acoustic Parameters of Ni $(NO_3)_2$ in Glycol + Water At 303.15 K.

Conc^n. mol dm^{-3}	U m sec^{-1}	B_s× 10^{-11} cm^2 dyne^{-1}	W	R	Z×10^{-5} cm^2 dyne^{-1}	L_f × 10^{-11}	□$_k$× 10^{-8}
10% Glycol + Water							
0.1000	1587	3.8962	36.6213	150.9612	16.1725	7.7785	-3606.64
0.0750	1582	3.9264	36.3909	150.6966	16.0990	7.8387	-4741.65
0.0500	1577	3.9569	36.1612	150.4321	16.0255	7.8996	-7004.29
0.0250	1572	3.9877	35.9323	150.1656	15.9523	7.9611	-13782.2
0.0100	1567	4.0166	35.7040	149.8155	15.8880	8.0188	-33068.8
0.0075	1561	4.0481	35.4311	149.2626	15.8250	8.0817	-40227.7
0.0050	1556	4.0748	35.2045	148.8070	15.7719	8.1349	-55500.6
0.0025	1551	4.1017	34.9786	148.3489	15.7191	8.1886	-101269
0.0010	1545	4.1340	34.7085	147.7881	15.6569	8.2530	-222373
0.0000	1541	4.1557	34.5290	147.4139	15.6155	8.2964	-3606.64
20% Glycol + Water							
0.1000	1617	3.7014	38.0189	151.6979	16.7082	7.3894	-6166.98
0.0750	1612	3.7295	37.7841	151.4383	16.6335	7.4456	-8182.15
0.0500	1607	3.7580	37.5501	151.1782	16.5589	7.5024	-12206.3
0.0250	1602	3.7867	37.3168	150.9176	16.4844	7.5598	-24266.5
0.0100	1597	3.8137	37.0842	150.5728	16.4192	7.6136	-59476.1
0.0075	1596	3.8192	37.0378	150.5067	16.4058	7.6246	-78875.7
0.0050	1591	3.8436	36.8061	150.0489	16.3529	7.6733	-113979
0.0025	1586	3.8684	36.5751	149.5984	16.2992	7.7228	-219032
0.0010	1581	3.8932	36.3449	149.1393	16.2465	7.7724	-524253
0.0000	1576	3.9182	36.1153	148.6759	16.1942	7.8222	-6166.98
30% Glycol + Water							
0.1000	1661	3.4639	40.1161	153.8726	17.3807	6.9153	-9105.68
0.0750	1654	3.4981	39.7787	153.4375	17.2833	6.9837	-12017.7
0.0500	1647	3.5329	39.4427	153.0029	17.1860	7.0531	-17830.5
0.0250	1640	3.5681	39.1081	152.5642	17.0893	7.1233	-35255.7
0.0100	1633	3.6018	38.7750	152.0411	17.0020	7.1905	-86268.4
0.0075	1630	3.6155	38.6327	151.7831	16.9684	7.2181	-113521
0.0050	1627	3.6294	38.4906	151.5248	16.9348	7.2457	-168011
0.0025	1623	3.6478	38.3016	151.1738	16.8907	7.2825	-329646
0.0010	1621	3.6571	38.2072	151.0003	16.8685	7.3011	-816297
0.0000	1620	3.6618	38.1601	150.9154	16.8572	7.3105	-9105.68

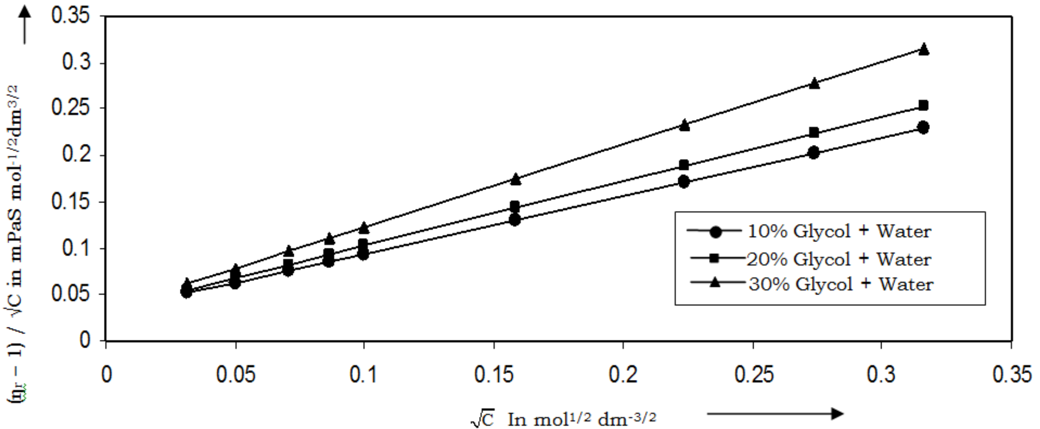

Fig. 1: Plot Of (H$_R$ – 1) /√C vs. √C of Nickel (II) Nitrate in Glycol + Water At 303.15 K

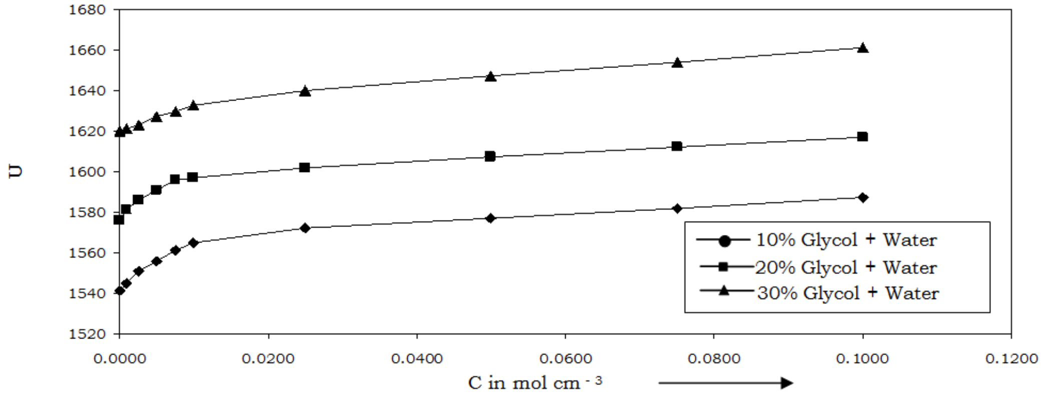

Fig. 2: Plot of U vs. √C of Nickel (II) Nitrate in Glycol + Water At 303.15 K

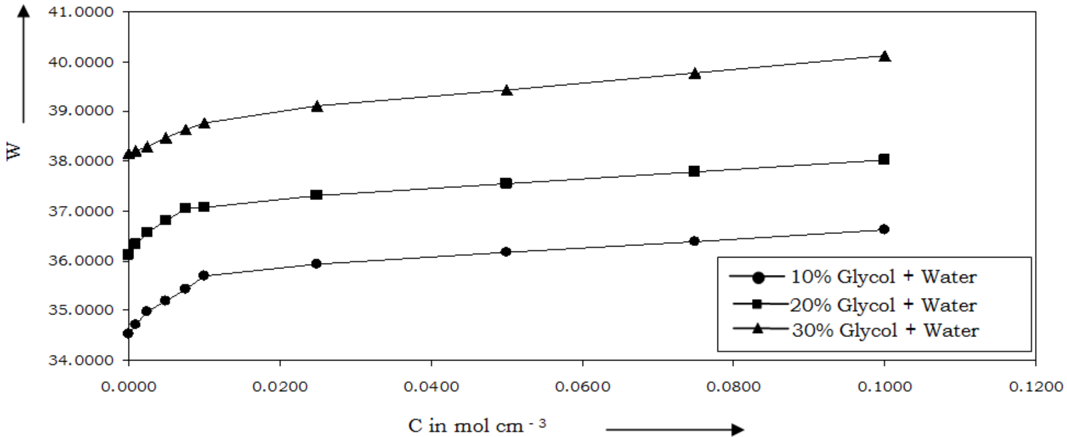

Fig. 3: Plot of W vs. √C of Nickel (II) Nitrate in Glycol + Water At 303.15 K

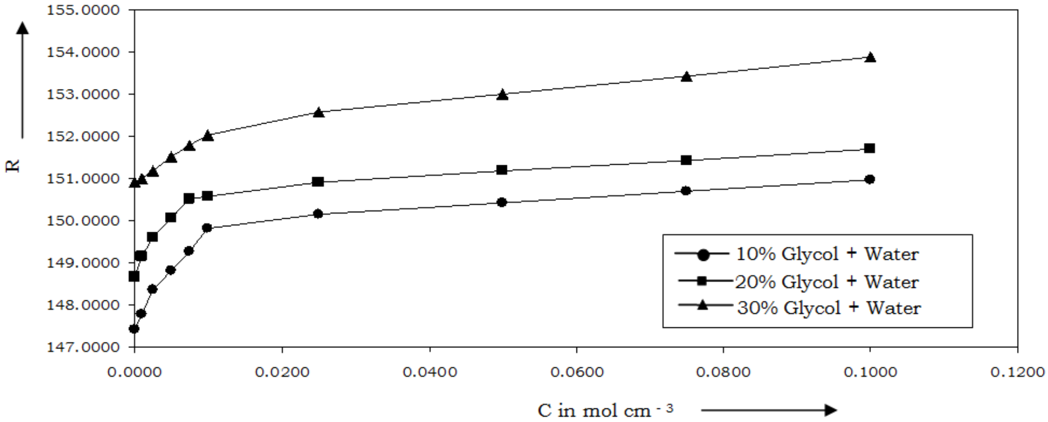

Fig. 4: Plot of R vs. √C of Nickel (II) Nitrate in Glycol + Water At 303.15 K

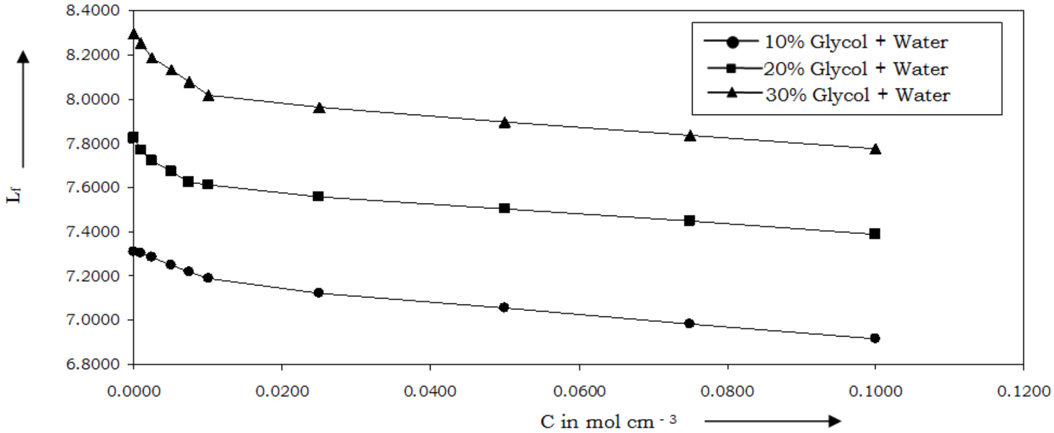

Fig. 5: Plot of L_f vs. √C of Nickel (II) Nitrate in Glycol + Water At 303.15 K

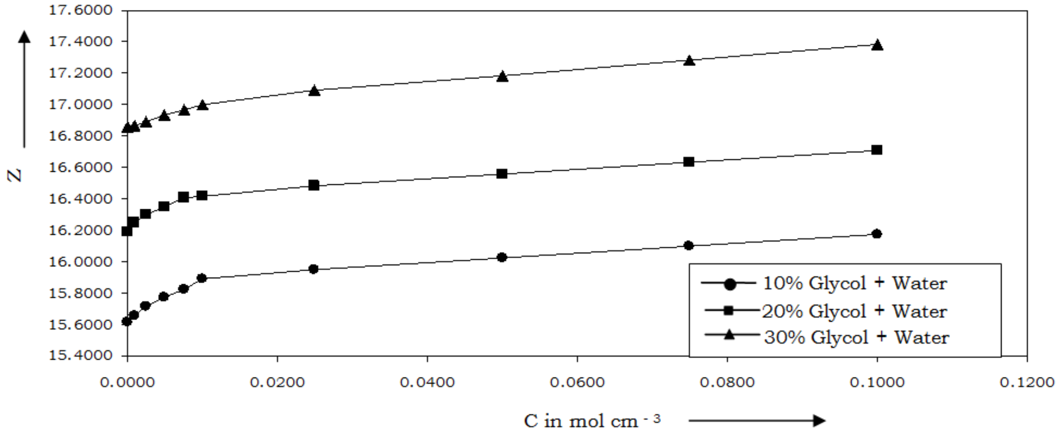

Fig. 6: Plot of Z vs. √C of Nickel (II) Nitrate in Glycol + Water At 303.15 K

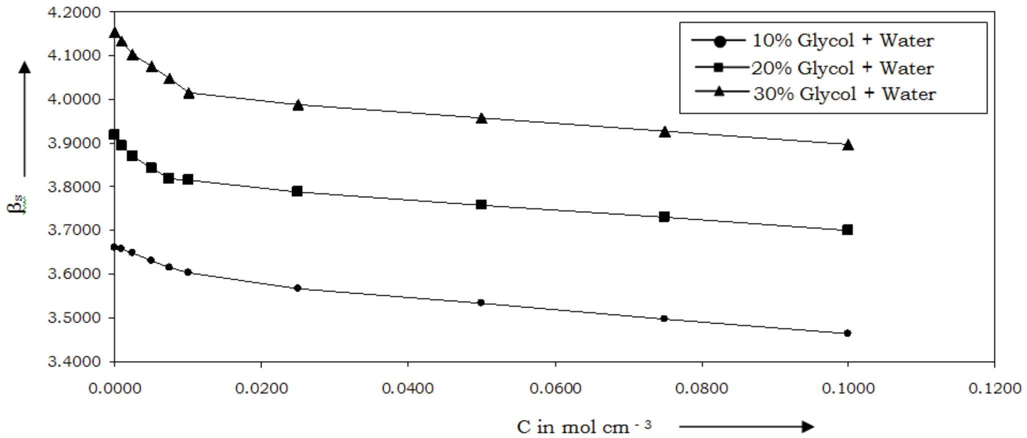

Fig. 7: Plot of Bs vs. √C of Nickel (II) Nitrate in Glycol + Water At 303.15 K

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