Ultrasonic Studies on Molecular Interaction and Physico-Chemical studies of Ca(NO$_3$)$_2$ in Aqueous Glycerol as solvent at 303.15K

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Abstract

Various acoustic parameters like isentropic compressibility (β_s), intermolecular free length (L$_f$), apparent molar volume (ϕ), apparent molar compressibility (ϕ_k), molar compressibility (w), molar sound velocity (R), acoustic impedance (z) of Ca(NO$_3$)$_2$ in 10%,20%,30% and Glycerol+water at 303.15 K have been determined from ultrasonic velocity (V), 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, Glycerol + water) when the solute is added to it.

Introduction

Ultrasonic Velocity measurements are helpful to study the ion-solvent interactions in aqueous and non-aqueous solutions. Ultrasound has been extensively used to determine the ion solvent interactions in aqueous solution containing electrolytes. In solution of ionic solute the attraction between the solute and solvent is essentially of ion–dipole interaction depends mainly on ion size and polarity of the solvent. The strength of ion-dipole attraction is directly proportional to the size of the ion, charge and magnitude of the dipole, but inversely proportional to the distance between the ion and the dipolar molecule. The dissolution of electrolyte in a solvent causes a volume contraction due to interaction between ions and solvent molecules and this may influence other acoustical properties of solution. In recent years, the studies of acoustical properties of aqueous mixed electrolytic solutions have been found to be useful in understanding the specific ion-ion and ion-solvent interactions in solutions. The accurate measurement of density, viscosity, apparent molar volume, Ultrasonic velocity and

hence the derived parameters such as molar compressibility, apparent molar compressibility will give significant information regarding the state of affairs in a solution. The interaction helps in better understanding of the types of solute and solvent *i.e.* whether the added solute modifies or distorts the structure of the solvent. Partial molar volumes of electrolytes provide valuable information about the ion-ion and ion-solvent interactions in ionic solutions. The addition of organic solvent to an aqueous solution of electrolyte brings about the change in ion solvation that often results in a large change in the reactivity of dissolved electrolyte. The use of Glycerol + water mixtures (10%, 20% &30%) has attracted much attention in recent years as solvent in the study of physico-chemical properties of electrolytic solutions. The present work reflects the ion-ion, ion-solvent and solvent-solvent interaction of $Ca(NO_3)_2$ solution in 10%,20%, and 30% Glycerol +water mixture[1].

Experimental

All the chemicals used in this present research work are spectroscopic reagent (SR) and analytical reagent (AR) grades of minimum assay of 99.9% obtained from E-merck, Germany and Sd Fine Chemicals, India, which are used as such without further purification. Water used in these experiments was deionized and distilled prior to making solutions. Required amount of water and Glycerol were taken to prepare the composition of binary mixtures (10%, 20% & 30%) in a clean dry conical flask with a ground stopper. The required quantity of Calcium Nitrate for a given molarity was dissolved in binary mixture of aqueous Glycerol and similar procedure has been adopted for different molarities. For each concentration,

the mass of Calcium Nitrate can be measured using electronic digital balance having an accuracy ±0.1 mg.(Model:SHIMADZU AX200). The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ±0.01 kg m^{-3}. An Ostwald's Viscometer (10ml Capacity) was used for the Viscosity measurement and efflux time was determined using a digital Chronometer to within ±0.01s. An ultrasonic interferometer having the frequency 5MHz (MITTAL ENTERPRISES, NEW DELHI, MODEL F-81) with an overall accuracy of ±0.1% has been used for ultrasonic velocity measurement. An electronically digital operated constant temperature bath (RAAGA INDUSTRIES) has been used to circulate water through the double walled measuring cell made of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ±0.1K.

Results and Discussion

The experimental datas of density (ρ) relative viscosity (η_r) and apparent molar volume (Φ) for the solute in different concentration of the solvent at 303.15 K are noted in Table 1. The viscosity A and B coefficients were calculated from the Jones-Dole equation. $\eta_r = 1 + A\sqrt{c} + Bc$

Where $\eta_r = (\eta/\eta_o)$, η and η_o are the viscosities of the solution and solvent respectively and c is the molal concentration of the solute. A is determined by the ionic attraction theory of Falkenhagen-Vernon and therefore also called Falkenhagen coefficient, B or Jones-Dole coefficient is an empirical constant determined by ion-solvent interactions. The Values of A and B are recorded in Table 2. From the result it is clear that the [2]relative viscosity (η_r) increases

with the increase in volume percentage of Glycerol. Such characteristic indicates the more extent of H-bonding of Glycerol with H_2O with the increase in volume percentage of Glycerol. With the increase in concentration of the solute the relative viscosity increases which is in good agreement with Widedmann and Coworkers[3].

Table 1. Physical properties of $Ca(NO_3)_2$ of different concentration in
10%, 20% and 30% Glycerol + water at 303.15K

Concentration		η_r	ρ gm ml^{-1}	ϕ cm^{3}mol^{-1}
i)	**10% Glycerol+water**			
	0.1000	1.01116	1.0493241	110.9828
	0.0750	1.00945	1.0328407	110.60998
	0.0500	1.00756	1.0163424	110.16774
	0.0250	1.00517	0.9998257	109.59140
	0.0100	1.00319	0.9899037	109.08000
	0.0075	1.00273	0.9882489	108.96210
	0.0050	1.00220	0.9865935	108.8225
	0.0025	1.00155	0.9849376	108.64000
	0.0000	-	0.9832808	108.2000
ii)	**20% Glycerol+water**			
	0.1000	1.01135	1.0371550	113.81443
	0.0750	1.00961	1.0207070	113.43736
	0.0500	1.00767	1.0042442	112.99010
	0.0250	1.00527	0.9877629	112.40721
	0.0100	1.00320	0.9778624	111.89000
	0.0075	1.00275	0.9762108	111.77076
	0.0050	1.00222	0.9745590	111.62932
	0.0025	1.00156	0.9729066	111.44500
	0.0000	-	0.9712534	111.00000
iii)	**30% Glycerol+water**			
	0.1000	1.01170	1.0232244	126.94605
	0.0750	1.00997	1.0068121	126.56475
	0.0500	1.00789	0.9903849	126.11246
	0.0250	1.00536	0.9739393	125.52302
	0.0100	1.00326	0.9640601	125.00000
	0.0075	1.00281	0.9624124	124.87942
	0.0050	1.00226	0.9607641	124.73640
	0.0025	1.00158	0.9591153	124.55000
	0.0000	-	0.9574657	124.10000

Table 2. limiting apparent molar volume (ϕ), limiting slope (S_v), A&B for
Ca(NO$_3$)$_2$ in 10%, 20%, 30% Glycerol + water at 303.15 k

Parameter	10%	20%	30%
ϕ_0 (cm^3 mol^{-1})	108.200	111.000	124.100
S_v (cm$^{9/2}$ mol$^{-3/2}$)	8.8	8.9	9.0
A X 10^{-2} (mol$^{1/2}$ lt$^{1/2}$)	3.01	3.02	3.05
B (mol^{-1} lt)	0.41	0.45	0.53

The data obtained have been found to agree with the [4]Masson's equation as the plot of ϕ vs $c^{1/2}$ is linear $\phi = \phi_0 + s_v\, c^{1/2}$

The values of the limiting apparent molar volume ϕ_0 obtained from the extrapolation of the above plot to zero concentration. The limiting slope s_v is a constant dependent on charge and salt type and can be related ion –ion interaction. The values of ϕ_0 and s_v are listed in Table 2. The limiting slope (s_v) is positive suggesting ion-ion interaction. This increases with the increase in non- aqueous solvent. The increase in ϕ_0 with increase in Glycerol content may be attributed to low surface.

The apparent molar volume (ϕ) were determined from the equations

$$\phi = \frac{M}{\rho_0} - \frac{(r - r_0)10^3}{\rho_0 \cdot c}$$ and are noted in table 1.

Where M is the molecular wt. of the solute, ρ_0 is the density of the solvent, ρ is the density of the solution, c is the molar concentration of the solution. The data obtained have been found to agree with the [4]Masson's equation as the plot of ϕ vs $c^{1/2}$ is linear $\phi = \phi_0 + s_v\, c^{1/2}$.

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The [6,7]ultrasonic velocity(U),[8] isentropic compressibility(β_s) , Molar compressibility (w), Molar sound velocity (R), [9]Acoustic impedance (Z), inter molecular free length (L$_f$) and Apparent molar compressibility (ϕ_k) of Ca(NO$_3$)$_2$ in 10%,20% and 30% Glycerol + H$_2$O at 303.15K are recorded in the Table 3. The values of U, W, R, ϕ_k increases and β_s, Z, L$_f$ decreases in Glycerol content in the solvent, suggest the powerful interaction between Glycerol and water. The increase in value of U, Z, ϕ_k and decrease in values of β_s, w, R, L$_f$ with the increase in concentration of the solute represents the decrease in cohesive force. This decrease in co-hesive force is due to the structure breaking nature of the solute. The

Table 3. Variation of U, β_s, W ,R ,Z, L and ϕ_k with concentration of $Ca(NO_3)_2$
in 10%, 20% and 30% Glycerol + water at 303.15K

Conc. Mole dm^{-3}	U m/sec	$\beta_s \times 10^{-2}$ cm^2 $dyne^{-1}$	$W \times 10^5$	R	Z cm^2 $dyne^{-1}$	L_f	ϕ_k
10% Glycerol + water							
0.1000	1552	39.56460	11.65956	62.85258	1526.052	0.000629	-0.00031
0.0750	1549	40.35191	11.73371	64.06585	1523.102	0.000635	-0.00023
0.0500	1546	41.16621	11.79417	65.32291	1520.152	0.000642	-0.00027
0.0250	1542	42.06363	11.87826	66.64109	1516.219	0.000649	-0.00032
0.0100	1541	42.54040	11.92345	67.4356	1515.236	0.000652	-0.00045
0.0075	1540	42.66698	11.92512	67.58201	1514.252	0.000653	-0.00054
0.0050	1536	42.96146	11.90865	67.77306	1510.319	0.000655	-0.00049
0.0025	1535	43.08984	11.89236	68.05422	1509.336	0.000657	-0.00044
0.0000	1534	43.21868	11.91240	68.53324	1508.353	0.000657	-
20% Glycerol + water							
0.1000	1561	39.56863	11.73241	64.61596	1516.127	0.000629	-0.00028
0.0750	1558	40.36124	11.78754	65.89268	1513.213	0.000635	-0.00021
0.0500	1556	41.12834	11.81373	67.20235	1511.270	0.000642	-0.00024
0.0250	1554	41.92231	11.89651	68.09967	1509.228	0.000648	-0.00028
0.0100	1552	42.45599	11.91547	68.35888	1507.385	0.000652	-0.00041
0.0075	1552	42.52780	11.93643	68.49402	1507.385	0.000653	-0.00048
0.0050	1551	42.65488	11.95749	68.64447	1506.414	0.000654	-0.00044
0.0025	1550	42.78242	11.95951	68.79552	1505.443	0.000654	-0.00041
0.0000	1550	42.85524	11.97521	65.51985	1505.443	0.000655	-
30% Glycerol + water							
0.1000	1571	39.54835	12.73671	65.51523	1504.179	0.000629	-0.00024
0.0750	1567	40.44955	12.79547	66.83908	1500.349	0.000636	-0.00021
0.0500	1564	41.12824	12.83319	68.19785	1497.476	0.000642	-0.00022
0.0250	1560	41.92231	12.86927	69.14825	1493.646	0.000645	-0.00025
0.0100	1557	42.45599	12.89537	69.43031	1490.774	0.000654	-0.00039
0.0075	1555	42.52780	12.91435	69.59790	1488.859	0.000656	-0.00041
0.0050	1555	42.65488	12.93780	69.73728	1488.859	0.000656	-0.00038
0.0025	1554	42.85524	12.97157	69.89239	1487.902	0.000657	-0.00035
0.0000	1554	42.78242	12.95573	69.77221	1487.902	0.000657	-

H-bond exists between Glycerol and H_2O is disrupted by the solute molecule and there by formation of new bonding between solute and solvent molecules has occurred[10-12].

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