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Physico-Chemical and Ultrasonic studies of Cobalt Nitrate in Aqueous Ethanol 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 $Co(NO_3)_2$ in 10%,20%,30% and Ethanol+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, Ethanol + 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 Ethanol + 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 $Co(NO_3)_2$ solution in 10%, 20%, and 30% Ethanol + water mixture[1,2].

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 Ethanol 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 Cobalt Nitrate for a given molarity was dissolved in binary mixture of aqueous Ethanol and similar procedure has been adopted for different molarities. For each concentration, the mass of Cobalt 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 data 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 $\eta_r = (\eta/\eta_0)$, η and η_0 are the viscosities of the solution and solvent respectively and c is the molar 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 Ethanol. Such characteristic indicates the more extent of H-bonding of Ethanol with H_2O with the increase in volume percentage of Ethanol. 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 $Co(NO_3)_2$ of different concentration in 10%, 20% and 30% Ethanol + water at 303.15K

Concentration η_r	ρ	ϕ gm ml^{-1}	cm^{3}mol^{-1}
i) 10% Ethanol+water			
0.1000	1.0773	1.0069	109.8196
0.0750	1.0591	1.0014	109.4552
0.0500	1.0406	0.9958	109.0230
0.0250	1.0216	0.9902	108.4598
0.0100	1.0097	0.9868	107.9600
0.0075	1.0076	0.9863	107.8448
0.0050	1.0055	0.9857	107.7081
0.0025	1.0032	0.9851	107.5300
0.0010	1.0016	0.9848	107.3720
ii) 20% Ethanol+water			
0.1000	1.0816	0.9960	113.6828
0.0750	1.0623	0.9905	113.3100
0.0500	1.0427	0.9850	112.8677
0.0250	1.0227	0.9795	112.2914
0.0100	1.0102	0.9761	111.7800
0.0075	1.0080	0.9756	111.6621
0.0050	1.0070	0.9751	111.5223
0.0025	1.0033	0.9745	111.3400
0.0010	1.0017	0.9741	111.1783
iii) 30% Ethanol+water			
0.1000	1.0849	0.9805	115.7725
0.0750	1.0647	0.9750	115.3743
0.0500	1.0444	0.9696	114.9019
0.0250	1.0236	0.9640	114.2863
0.0100	1.0106	0.9607	113.7400
0.0075	1.0083	0.9602	113.6141
0.0050	1.0059	0.9596	113.4647
0.0025	1.0034	0.9590	113.2700
0.0010	1.0017	0.9587	113.0973

Table 2. limiting apparent molar volume (ϕ), limiting slope (S_v), A&B for $Co(NO_3)_2$ in 10%, 20%, 30% Ethanol + water at 303.15 k

Parameter	10%	20%	30%
ϕ_0 ($cm^3\ mol^{-1}$)	107.1341	110.9431	112.8232
S_v ($cm^{9/2}\ mol^{-3/2}$)	0.881	0.894	0.907
A X 10^{-2} ($mol^{1/2} lt^{1/2}$)	3.01	3.03	3.06
B (mol^{-1} lt)	0.42	0.47	0.56

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 sv 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 Ethanol content may be attributed to low surface.

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

Conc. Mole dm^{-3}	U m/sec	β_s x 10^{-11} cm^2 $dyne^{-1}$	W x 10^5	R x 10^2 CGS unit	Z x 10^{-4} cm^2 $dyne^{-1}$	L_f	ϕ_k x 10^{-14} CGS unit
10% Ethanol + water							
0.1000	1558.3	4.0900	5.1790	127.0404	15.6902	4.0375	-1.3997
0.0750	1557.6	4.1160	5.2027	127.7199	15.5978	4.0503	-1.4016
0.0500	1556.5	4.1450	5.2267	128.4079	15.4996	4.0645	-1.5003
0.0250	1555.3	4.1749	5.2509	129.1009	15.4006	4.0792	-1.9693
0.0100	1553.5	4.1990	5.2646	129.4957	15.3299	4.0909	-3.3328
0.0075	1553.0	4.2039	5.2664	129.5475	15.3172	4.0933	-3.5583
0.0050	1551.5	4.2146	5.2677	129.5846	15.2931	4.0985	-4.0064
0.0025	1550.5	4.2226	5.2695	129.6356	15.2740	4.1024	-5.3438
0.0010	1550.0	4.2266	5.2704	129.6612	15.2644	4.1043	-7.3946
0.0000	1549.0	4.2329	5.2703	129.6596	15.2515	4.1074	....

20% Ethanol + water							
0.1000	1596.6	3.9389	5.2639	129.4742	15.9017	3.9622	-1.3117
0.0750	1596.2	3.9625	5.2886	130.1833	15.8104	3.9740	-1.3619
0.0500	1595.5	3.9881	5.3132	130.8911	15.7157	3.9869	-1.5624
0.0250	1594.7	4.0146	5.3380	131.6041	15.6201	4.0001	-1.8927
0.0100	1593.9	4.0327	5.3532	132.0396	15.5578	4.0091	-4.0609
0.0075	1593.5	4.0367	5.3552	132.0970	15.5462	4.0111	-3.2458
0.0050	1592.0	4.0464	5.3561	132.1233	15.5236	4.0159	-3.5682
0.0025	1591.0	4.0561	6.5439	132.1769	15.5043	4.0664	-4.8857
0.0010	1590.0	4.0607	5.3589	132.2035	15.4882	4.0230	-6.4026
0.0000	1588.0	4.0716	5.3576	132.1684	15.4663	4.0284	....
30% Ethanol + water							
0.1000	1604.8	3.9601	5.3430	131.7468	15.7351	3.9729	-1.4412
0.0750	1604.0	3.9865	5.3680	132.4680	15.6390	3.9860	-1.5418
0.0500	1603.0	4.0137	5.3927	133.1781	15.5427	3.9996	-1.7157
0.0250	1602.0	4.0420	5.4186	133.9238	15.4433	4.0137	-2.2540
0.0100	1601.0	4.0610	5.4336	134.3559	15.3808	4.0231	-3.9615
0.0075	1600.5	4.0656	5.4355	134.4119	15.3680	4.0254	-4.4065
0.0050	1600.0	4.0707	5.4379	134.4819	15.3536	4.0279	-4.4160
0.0025	1599.0	4.0783	5.4399	134.5380	15.3344	4.0317	-5.6747
0.0010	1598.0	4.0847	5.4404	134.5520	15.3200	4.0349	-7.3815
0.0000	1596.0	4.0957	5.4393	134.5211	15.2980	4.0403	....

The apparent molar volume (ϕ) were determined from the equations $\phi = \frac{M}{\rho_0} - \frac{(r - r_0)10^3}{\rho_0 \, . \, c}$ 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 $\phi = \phi_0 + s_v c^{1/2}$. 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 Ethanol content may be attributed due to low surface[5].

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 $Co(NO_3)_2$ in 10%,20% and 30% Ethanol + H_2O 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 Ethanol content in the solvent , suggest the powerful interaction between Ethanol 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 H-bond exists between Ethanol 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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