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Ultrasonic and Physico-Chemical studies of Magnesium Chloride in aqueous Ethanol (10%, 20% and 30%) 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 $MgCl_2$, in 10%, 20% and 30% 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 (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[1]. 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 interaction 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 acoustic 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 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[2,3]. The present work reflects the ion-ion, ion-solvent and solvent-solvent interaction of $MgCl_2$ solutions in 10%, 20%, and 30% Ethanol + water mixture.

Experimental

The Magnesium Chloride used in the present work were analytical reagent (AR) grades with a minimum assay of 99.9% obtained from S.D Fine Chemicals (India) without further purification. In all the measurements various concentrations of the solvent mixtures were prepared in terms of molarity varied from 0.1000 to 0.0010. The densities of pure liquids and liquid mixtures were determined using Pycnometer at 303.15K. An Oswald's viscometer with 10ml. Capacity was used for the viscosity measurements of pure liquids and liquid mixtures. The viscometer was calibrated with fresh conductivity water immersed in a water bath and that can be operated at various temperatures. The flow time of the solvent and the flow time of solutions were measured with a digital stop clock with an accuracy of 0.01S (RACER HS-10W). For each concentration the mass of Magnesium Chloride was measured using electronic digital balance having an accuracy ±0.1mg. (Model : SHIMADZU AX200). 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.

Theory and Calculations :

Using the measured data all the parameters have been calculated using the standard relations. Isentropic compressibility $\beta_s = U^{-2}.\ \rho^{-1}$

The apparent molar compressibility has been calculated from the relation

$$\phi_k = \frac{1000\beta_s}{C} - \frac{\beta_s}{\rho^{-1}} \frac{(1000\rho - M)}{c}$$

Where β_s and $\beta^0{}_s$ are the isentropic compressibility of the solution and solvent respectively. ρ and ρ_0 are the density of solution and solvent respectively. C is the molar concentration of the solution and M is the molecular mass of solute.

The Apparent molar volume (ϕ) is calculated by using the relation

$$\phi = \frac{M}{\rho_0} + \frac{(\rho - \rho)}{\rho_0} \times \frac{10^3}{C}$$

Where ρ and ρ_0 are the density of solution and solvent. C is the molar concentration and M is the molecular mass of solute.

The viscosity A and B coefficients for the electrolytes in 10%, 20% and 30% Ethanol + water solutions were calculated from the Jones-Dole equation.

$$\frac{\eta}{\eta_o} = \eta_r = 1 + AC^{1/2} + BC$$

Where η and η_0 are the viscosities of solution and solvent respectively and C is the molar concentration of the solution. 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.

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.

$$\eta_r = 1 + A\sqrt{c} + Bc$$

The values of A and B are recorded in Table 2. From the result it is clear that the 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.

Table 1. Physical properties of $MgCl_2$ of different concentration in 10%, 20% and 30% Ethanol + water at 303.15K

Concentration	η_r	ρ (gm cm^{-3})	ϕ (cm^{3}mol^{-1})
i) **10% Ethanol+water**			
0.1000	1.0827	1.023205	114.7213
0.0750	1.0620	1.020740	112.4621
0.0500	1.0382	1.018273	110.0357
0.0250	1.0198	1.015803	107.9131
0.0100	1.0085	1.014319	105.7314
0.0075	1.0077	1.014072	103.5781
0.0050	1.0053	1.013824	101.4039
0.0025	1.0030	1.013577	99.3352
0.0010	1.0027	1.013428	97.4713
ii) **20% Ethanol+water**			
0.1000	1.0846	1.037286	122.6178
0.0750	1.0655	1.034854	120.4426
0.0500	1.0395	1.032419	116.7013
0.0250	1.0209	1.029982	114.9007

0.0100	1.0087	1.028518	112.8175
0.0075	1.0081	1.028274	110.6092
0.0050	1.0055	1.028030	108.4751
0.0025	1.0032	1.027786	106.3472
0.0010	1.0030	1.027639	104.5021
iii) 30% Ethanol+water			
0.1000	1.0893	1.050064	136.8105
0.0750	1.0672	1.047691	134.8001
0.0500	1.0403	1.045315	132.3502
0.0250	1.0215	1.042937	130.2731
0.0100	1.0090	1.041508	128.4621
0.0075	1.0083	1.041270	125.6355
0.0050	1.0058	1.041032	123.4028
0.0025	1.0039	1.040793	121.2357
0.0010	1.0032	1.040650	118.4136

Table 2. Limiting apparent molar volume (ϕ_0), limiting slope (S_v), A & B for $MgCl_2$ in 10%, 20%, 30% Ethanol + water at 303.15 k

Parameter	10%	20%	30%
ϕ_0 (cm^3 mol^{-1})	95.2003	102.7158	117.2672
S_v ($cm^{9/2}$. $mol^{-3/2}$)	5.73	5.98	6.09
A X 10^{-2} ($mol^{1/2}$ $L^{1/2}$)	3.55	3.67	3.78
B (mol^{-1} L)	0.757	0.782	0.829

The data obtained have been found to agree with the 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 to 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 $MgCl_2$ in 10%, 20% and 30% Ethanol + water at 303.15K

Conc. Mol. dm^{-3}	U m/sec	$\beta_s \times 10^{-12}$ cm^2 dyne^{-1}	W x 10^5	R	Z x 10^{-5} cm^2. dyne^{-1}	$L_f \times 10^{-6}$ (m)	$\phi_k \times 10^{-8}$ cm^2.dyne^{-1}
10% Ethanol + water							
0.1000	1568	39.7507	3559.53	1351.14	1.6044	6.3048	-2.2120
0.0750	1564	40.6508	4952.57	1353.25	1.5964	6.3213	-2.9514
0.0500	1560	40.3540	3569.08	1355.37	1.5885	6.3524	-3.3018
0.0250	1555	40.7127	3573.24	1357.21	1.5796	6.38065	-5.2527
0.0100	1553	40.8773	3576.40	1358.61	1.5752	6.3935	-11.6107
0.0075	1550	40.0457	3575.17	1358.07	1.5718	6.4066	-13.2635
0.0050	1545	41.3219	3572.62	1356.94	1.5663	6.4282	-14.4124
0.0025	1539	41.6549	3569.39	1355.52	1.5599	6.4541	-15.5886
0.0010	1535	41.8784	3567.19	1354.53	1.5556	6.4713	-16.7438
20% Ethanol + water							
0.1000	1602	37.6584	3538.43	1341.80	1.6596	6.1366	-1.2826
0.0750	1599	37.7941	3544.93	1344.68	1.6547	6.1477	-1.5568
0.0500	1598	37.9307	3551.46	1347.57	1.6498	6.1588	-2.1030
0.0250	1596	38.1158	3557.39	1350.19	1.6439	6.1738	-3.5473
0.0100	1595	38.2179	3561.09	1351.83	1.6405	6.1821	-7.9694
0.0075	1590	38.4678	3558.62	1350.73	1.6349	6.2022	-7.3209
0.0050	1585	38.7200	3556.14	1349.64	1.6995	6.2225	-5.9779
0.0025	1582	38.8763	3554.94	1349.10	1.6259	6.2351	-5.7852
0.0010	1580	38.9803	3554.09	1348.73	1.6237	6.2434	-4.1827
30% Ethanol + water							
0.1000	1651	34.9373	3533.03	1339.41	1.7337	5.9108	-1.6879
0.0750	1646	35.2296	3536.82	1341.08	1.7245	5.9355	-1.8891
0.0500	1640	35.5684	3540.01	1342.50	1.7143	5.9639	-2.1983
0.0250	1634	35.9118	3543.22	1343.92	1.7042	5.9927	-3.1073
0.0100	1630	36.1378	3544.90	1344.66	1.6977	6.0114	-5.6337
0.0075	1627	36.2795	3543.73	1344.15	1.6942	6.0233	-5.6503
0.0050	1625	36.3772	3543.18	1343.90	1.6917	6.0314	-6.5634
0.0025	1622	36.5203	3542.03	1343.38	1.6882	6.0432	-7.4853
0.0010	1620	36.6155	3541.17	1343.01	1.6858	6.0511	-9.3185

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 $\phi = \phi_0 + s_v c^{1/2}$. 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.

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 $MgCl_2$ 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.

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