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ULTRASONIC STUDIES OF $MgBr_2$ IN GLYCEROL + WATER SOLVENT AT 303.15 K

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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 $MgBr_2$ 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

The dissolution of electrolyte in various solvents is responsible for structure maker or structure breaker [1]. Viscosity and density data leads an insight in to the state of association of the solute and the extent of interaction of the solute with the solvent. The present work reflects the ion-ion, ion-solvent and solvent-solvent interaction of $MgBr_2$ solution in 10%, 20%, and 30% Glycerol + water.

Experiment

The solvents used were purified by appropriate method. GLYCEROL used was ANALAR sample and water was triple distilled. Purity was about 99.9% which was in good agreement

with the standard values of density, viscosity etc. The solvents of different GLYCEROL content were prepared by taking required volume of GLYCEROL in distilled water. For the preparation of different concentration of solution, the required amount of $MgBr_2$ was weighed and dissolved in a 250 ml measuring flask.

In the present work the ultrasonic velocity of the solution was measured by a commercially available ultrasonic interferometer of frequency 5 MHZ manufactured by Mitall Enterprisers.

Results and discussion

The experimental data's of density (ρ) and relative viscosity (η_r) for the solute in different concentration of the solvent at 303.15K are noted in Table 1.

From the result it is clear that the relative [2] 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 Widemann and coworkers [3].

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

$$\phi = \frac{M}{\rho_0} - \frac{(r - r_0) \times 10^3}{\rho_0 c}$$ 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.

Observation

Table 1. Physical properties of $MgBr_2$ different concentration in 10%, 20% and 30% Glycerol + water at 303.15K

Concentration	η_r **Kg.m^{-1}.s^{-1}**	ρ **gm ml^{-1}**	ϕ **cm^3 mol^{-1}**
(i) 10% Glycerol			
0.1000	1010.734	1.035736	20.26999
0.0750	1008.263	1.032107	20.22042
0.0500	1005.747	1.028476	20.26162
0.0250	1003.142	1.024843	20.08499
0.0100	1001.473	1.022661	20.01700
0.0075	1001.173	1.022297	20.00132
0.0050	1000.855	1.021933	19.98273
0.0025	1000.513	1.021570	19.85850
0.0010	1000.272	1.021351	19.93700
0.0000	1000.112	1.021206	
(ii) 20% Glycerol			
0.1000	1010.929	1.062312	21.05418
0.0750	1008.421	1.058717	21.00672
0.0500	1005.864	1.055120	20.95049
0.0250	1003.214	1.051521	20.87709
0.0100	1001.517	1.049360	20.81200
0.0075	1001.203	1.048999	20.79699
0.0050	1000.881	1.048639	20.77922
0.0025	1000.532	1.048278	20.75600
0.0010	1000.283	1.048062	20.73542
0.0000	1000.148	1.047918	
(iii) 30% Glycerol			
0.1000	1010.692	1.096267	23.08264

0.0750	1008.251	1.092745	23.03137
0.0500	1005.759	1.089222	22.97056
0.0250	1003.171	1.085695	22.89132
0.0100	1001.524	1.083577	22.82100
0.0075	1001.198	1.083224	22.80479
0.0050	1000.887	1.082871	22.78556
0.0025	1000.539	1.082518	22.76050
0.0010	1000.287	1.082306	22.73826
0.0000	1000.173	1.082164	

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

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.

Table 2. **Limiting apparent molar volume (ϕ), limiting slope (s_v) *A* and *B* for $MgBr_2$ in 10%, 20%, 30% Glycerol + water at 303.15K**

Parameter	10%	20%	30%
ϕ_0 (cm^3 mol^{-1})	19.9	20.7	22.7
s_v ($cm^{9/2}$ $mol^{-3/2}$)	1.17	1.12	1.21
$A \times 10^{-2}$ ($mol^{1/2}$ $lt^{1/2}$)	5.10	5.20	4.50
B (mol^{-1} lt)	8.00	8.90	10.40

The increase in ϕ_0 with increase in GLYCEROL content may be attributed to low surfaced charge density as a result of which the electrostatic attraction is more in a medium of low dielectric constant and hence ion-solvent interaction would also be more. The plot of $\frac{\eta_r - 1}{c^{1/2}}$ is linear, which is in good agreement with the Jones [5] – Dole equation

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

$$\frac{\eta_r - 1}{c^{1/2}} = 1 + Bc^{1/2}$$

the values of *A* and *B* are obtained from the graph and are recorded in Table 2.

Table 3. Variation of *U*, β, *W*, *R*, *Z*, *L* and ϕ_k with concentration of $MgBr_2$ in 10%, 20% and 30% Glycerol + water at 303.15 K

Conc.	U	$\beta \times 10^{-2}$	w	R	$Z \times 10^{-5}$	$L \times 10^{-4}$ m	ϕ_k

Mole dm^{-3}	**m/sec**	**cm^2 dyne^{-1}**			**cm^2 dyne^{-1}**		
10% Glycerol + water							
0.1000	1568	39.2698	2626.2997	1033.0608	1.62403	6.26656	– 1.70154
0.0750	1565	39.5591	2733.0184	1036.0316	1.61525	6.28960	– 1.81237
0.0500	1563	39.8004	2740.2856	1039.2462	1.60751	6.30867	– 2.12991
0.0250	1561	40.0440	2747.6036	1042.4852	1.59978	6.32803	– 3.07300
0.0100	1560	40.1808	2752.1248	1044.4864	1.59535	6.33883	– 5.99500
0.0075	1558	40.2984	2751.9556	1044.4116	1.59274	6.34810	– 6.35415
0.0050	1555	40.4685	2751.2798	1044.1126	1.58910	6.36149	– 6.02247
0.0025	1553	40.5872	2751.1061	1044.0356	1.58649	6.37081	– 7.08500
0.0010	1551	40.7006	2750.6964	1043.8478	1.58406	6.37970	– 5.90611
0.0000	1550	40.7590	2750.4265	1043.7348	1.58287	6.38428	
20% Glycerol + water							
0.1000	1606	36.4970	2686.0473	1015.2883	1.70607	6.04127	– 1.72435
0.0750	1603	36.7581	2692.4248	1018.1011	1.69712	6.06285	– 1.88851
0.0500	1600	37.0218	2698.8461	1020.9343	1.68819	6.08455	– 2.21134
0.0250	1596	37.3350	2704.8262	1023.5741	1.67823	6.11024	– 2.98176
0.0100	1595	37.4588	2709.1123	1025.4668	1.67373	6.12036	– 5.93386
0.0075	1592	37.6131	2708.4562	1025.1771	1.67064	6.13295	– 5.79073
0.0050	1589	37.7682	2707.7938	1024.8845	1.66628	6.14558	– 5.48991
0.0025	1587	37.8765	2707.6184	1024.8071	1.66361	6.15439	– 6.45799
0.0010	1585	37.9800	2707.1209	1024.5876	1.66117	6.16279	– 5.51243
0.0000	1584	38.0332	2706.9516	1024.5128	1.65990	6.16711	
30% Glycerol + water							
0.1000	1656	33.2631	2637.5807	993.94739	1.81542	5.76742	– 1.33393
0.0750	1654	33.4511	2643.9522	996.74937	1.80740	5.78369	– 1.47612
0.0500	1651	33.6814	2649.9052	999.36833	1.79831	5.80357	– 1.67589
0.0250	1647	33.9551	2655.4418	1001.8045	1.78814	5.82710	– 2.10110
0.0100	1646	34.0628	2659.4288	1003.5595	1.78357	5.83633	– 3.94135
0.0075	1644	34.1569	2659.2473	1003.4798	1.78082	5.84439	– 3.94837
0.0050	1643	34.2096	2659.5283	1003.6033	1.77915	5.84890	– 4.79043
0.0025	1641	34.3042	2659.3462	1003.5231	1.77644	5.85698	– 5.64058
0.0010	1640	34.3528	2659.3293	1003.5157	1.77498	5.86113	– 9.00642
0.0000	1638	34.4413	2658.7008	1003.2392	1.77258	5.86867	

The result reveals that the value of A increases in Glycerol content, which also supports the increase in electrostatics attraction in a medium of low dielectric constant and also the increase in ion solvent interaction. The increase in B values with increase in Glycerol content is due to large size of the solvent molecule and also the strong association between water and organic solvent through H-bonding.

The ultrasonic [6, 7] velocity (*U*), isentropic [8] compressibility (β_s), Molar compressibility (*w*), Molar sound velocity (*R*), Acoustic [9] impedance (*Z*), inter molecular free length (L_f) and Apparent molar compressibility (ϕ_s) of $MgBr_2$ in 10%, 20% and 30% GLYCEROL + H_2O at 303.15 K are recorded in the table 3.

The valued 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 cohesive force is due to the structure breaking nature of the solute. The H-bond exists between CLYCEROL and WATER is disrupted by the solute molecule and thereby formation of new bonding between solute and solvent molecules has occurred.

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