Acta Ciencia Indica, Vol. XLIV C, No. 4, 105 (2018)

ULTRASONIC STUDIES OF $MnSO_4$ IN METHANOL + WATER SOLVENT AT 303.15K

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RECEIVED : 6 May, 2018

Various acoustic parameters like isentropic compressibility (β_s), inter-molecular free length (L_f), Apparent molar volume (ϕ), apparent molar compressibility (ϕ_k), molar compressibility (w), molar sound velocity (R), acoustic impedance (z) of $CdSO_4$ in 10%, 20%, 30% and methanol + 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.*, methanol + water) when the solute is added to it.

INTRODUCTION

The dissolution of electrolytic 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 $MnSO_4$ solution in 10%, 20% and 30% methanol + water.

RESULTS AND DISCUSSION

The experimental datas of density (ρ) and relative viscosity (η_r) for the solute ($MnSO_4$) in different concentration of the solvent (10%, 20% and 30% methanol + water) at 303.15 K are noted in Table-1.

From the result it is clear that the [2] relative viscosity (η_r) increase in volume percentage of methanol. Such characteristic indicates the more extent of H-bonding of CH_3OH with H_2O with the increase in volume percentage of CH_3OH. With the increase in concentration of the solute the relative viscosity (η_r) increases which is in good agreement with Widedmann and coworkers [3].

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

$$\phi = \frac{M}{\rho_0} - \left[\frac{\rho - \rho_0}{\rho_0}\right] \times \left(\frac{10^3}{c}\right)$$

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.

Table 1. Physical properties of $MnSO_4$ of different concentration in 10%, 20% and 30% methanol + water at 303.15 K

Concentration	η_{r+}	ρ gm ml^{-1}	ϕ cm^3 mol^{-1}
(i) 10% methanol			
0.1000	1.01116	1.0493141	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% methanol			
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	1.00275	0.9762108	111.62932
0.0050	1.00222	0.9745590	111.62932
0.0025	1.00156	0.9729066	111.44500
0.0000	–	0.9712534	111.00000
(iii) 30% methanol			
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	124.1000

The data obtained have been found to agree with Masson's [4] 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. The values of ϕ_0 and S_v are listed in table 2.

Table 2. Limiting apparent molar volume (ϕ_0), limiting slope (S_v), A & B for $MnSO_4$ in 10%, 20% and 30% methanol + water at 303.15 K.

Parameter	10%	20%	30%
ϕ_0 (cm^9 mol^{-1})	108.200	111.000	124.100
S_v ($cm^{9/2}$ $mol^{-3/2}$)	8.8	8.9	9.0
A × 10^{-2} ($mol^{1/2}$ $lt^{1/2}$)	3.01	3.02	0.305
B (mol^{-1} lt)	0.41	0.45	0.53

Table 3. Variation of U, β_s, W, R, Z, L_r ϕ_k with concentration of $MnSO_4$ in 10%, 20% and 30% methanol + water at 303.15 K.

Conc. Mol. dm^{-3}	U m/sec.	$\beta_s \times 10^{-12}$ cm^2dyne^{-1}	W × 10^5	R	Z cm^2dyne^{-1}	I_a	ϕ_k
10% methanol + water							
0.1000	1552	39.56460	11.65956	62.85268	1526.052	0.000629	-0.00031
0.0750	1549	40.35191	11.73371	64.06585	1523.102	0.000635	-0.00023
0.5000	1546	41.16624	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
0.000	1534	43.21868	11.91240	68.53324	1508.353	0.000657	-
20% methanol+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
0.5000	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
0.000	1550	42.85524	11.97521	65.51985	1505.443	0.000655	-
30% methanol + 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
0.5000	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	42.52780	12.89537	69.43031	1490.774	0.000654	-0.00039
0.0075	1555	42.65488	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	42.78242	12.95573	69.77221	1487.902	0.000657	-0.00035
0.000	1554	42.85524	12.97157	69.89239	1487.902	0.000657	-

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 CH_3OH content may be attributed to low surface 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 $(\eta_r - 1)/c^{1/2}$ vs $c^{1/2}$ is linear, which is in good agreement with the [5]Jones – Dole equation

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

$$(\eta_r - 1) / c^{1/2} = A + Bc^{1/2}$$

The values of A and B are obtained from the graph and are recorded in table-2.

The result reveals that the value of A increases with the increase in CH_3OH content, which also supports the increase in electrostatic attraction in a medium of low dielectric constant and also the increase in ion solvent interaction. The increase in B values with increase in CH_3OH content is due to large size of the solvent molecule and also the strong association between water and organic solvent through H-bonding.

The [6, 7] ultrasonic velocity (U) [8], isentropic compressibility (β_s), Molar compressibility (w), Molar sound velocity (R) [9] Acoustic impendance (Z) intermolecular free length (L_f) and Apparent molar compressibility (ϕ_k) increases and β_s, Z, L_f decreases with the increase in CH_3OH content in the solvent, suggest the powerful interaction between CH_3CH and water.

The increase in values 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 exist between CH_3OH and H_2O is disrupted by the solute molecule and there by formation of new bonding between solute and solvent molecules has occurred.

Experiments

The solvents used were purified by appropriate method. CH_3OH 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 CH_3OH content were prepared by taking required volume of CH_3OH in distilled water. For the preparation of different concentration of solution, the required amount of $MnSO_4$ was weighed and dissolved in a 250 ml measuring task.

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

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