

# THE APPARENT MOLAL VOLUME OF SOLUTIONS OF MgCl<sub>2</sub>, MgBr<sub>2</sub> AND Mg(NO<sub>3</sub>)<sub>2</sub> IN DIOXANE + WATER AND GLYCOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

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RECEIVED : 6 May, 2018

From viscosity data,  $\phi$  of MgCl<sub>2</sub>, MgBr<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> at 10, 20 and 30% (w/w) of dioxane+water and glycol+water at 30°m, 35° and 40° have been calculated and from it ion solvent interaction has been inferred. It is of the order NO<sub>3</sub><sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> and dioxane+water > Glycol+water.

## INTRODUCTION

The apparent molar volume of MgCl<sub>2</sub>, MgBr<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> has been calculated from the density data within temperature range 30-40°C and Ion Solvent interaction have been inferred.

## MATERIALS AND METHODS

The salts used were 'E' Merck' extra pure varieties. The preparation of solvents, solutions and method of density measurements were the same as that of Das [1]. Buoyancy correction has been done for the calculation of density.

## DISCUSSION

The apparent molar volume ( $\phi$ ) calculated from the equation.

$$\phi = M/\rho_0 - [(\rho - \rho_0)/\rho_0] (10^3/C)$$

was found to vary linearly with C<sup>1/2</sup> i.e. fit in the empirical Masson's equation [2].

$$\phi = \phi^\circ + S_V C^{1/2}$$

where  $\varnothing^\circ$  is the limiting apparent molar volume. The limiting apparent molar volume  $\varnothing^\circ$ , thus obtained from the extrapolation of the linear plots of zero concentration for  $\text{MgCl}_2$ ,  $\text{MgBr}_2$  and  $\text{Mg}(\text{NO}_3)_2$  in dioxane+water and glycol+ water at different temperatures are given in table 1.

**Table 1.**  $\varnothing^\circ / \text{cm}^3, \text{mol}^{-1}$

|                            |    | D+W   |       |       | G+W   |       |       |
|----------------------------|----|-------|-------|-------|-------|-------|-------|
|                            |    | 10%   | 20%   | 30%   | 10%   | 20%   | 30%   |
| $\text{MgCl}_2$            | 30 | 29.34 | 28.15 | 29.42 | 28.13 | 26.93 | 28.44 |
|                            | 35 | 29.41 | 28.45 | 29.60 | 28.40 | 27.52 | 28.70 |
|                            | 40 | 29.94 | 28.85 | 29.84 | 28.90 | 27.94 | 29.09 |
| $\text{MgBr}_2$            | 30 | 30.80 | 32.15 | 38.14 | 28.42 | 39.93 | 37.12 |
|                            | 35 | 30.90 | 32.65 | 38.41 | 28.56 | 30.42 | 37.53 |
|                            | 40 | 31.21 | 32.95 | 38.72 | 29.96 | 30.94 | 38.22 |
| $\text{Mg}(\text{NO}_3)_2$ | 30 | 34.80 | 36.30 | 38.75 | 29.84 | 31.97 | 39.12 |
|                            | 35 | 35.00 | 36.50 | 39.00 | 30.22 | 32.23 | 39.54 |
|                            | 40 | 35.20 | 36.80 | 39.40 | 31.42 | 32.98 | 40.15 |

#### Dependence of $\varnothing^\circ$ on temperature :

The limiting apparent molar volume ( $\varnothing^\circ$ ) increase with increase in temperature for these three salts studied in all the solvents. The plot of  $\varnothing^\circ$  against 't' is found to be linear. The  $d\varnothing^\circ/dt$  also increase with the increase in dioxane glycol content, indicating some ion-solvent interaction. The order is Dioxane + water > Glycol + water. The reason is ion-solvent dipole interaction energy will lead to the breaking of the strong intermolecular hydrogen bonds and would lead to strong ion solvent interaction together with primary and secondary solvation depending upon the radius of the ion concerned.

#### The Limiting Slope ( $S_v$ ) :

The  $S_v$ , the limiting slope obtained from the plot of  $\varnothing^\circ$  vs  $C^{1/2}$  are recorded in Table 2. The  $S_v$  value is found to change little with the change in the dielectric constant. If the dielectric constant is not very high or it is fairly high as that of water and the ions are not large, the electrostatic ion-ion attraction will be appreciable and an anion will have strong influence on its neighbour even if association does not occur [3]. Ion association is expected in solvents of low dielectric constant and actual association is likely even at low concentration. This coupled with ion-solvent interaction seems to be responsible for the positive slopes of  $\varnothing^\circ$  Vs  $C^{1/2}$  plots in these systems. Moreover the plots of  $S_v$  vs wt% of organic solvent is linear. It is seen that this is mainly of the order  $D + W > GW^+$ .

#### Dependence of $\varnothing^\circ$ on organic solvent :

The increase in  $\varnothing^\circ$  with increase in organic solvent may be attributed due to the low surface charge density, as a result of which electrostatic attraction is more in a medium of low dielectric constant and hence ion solvent interaction will also be more and consequently  $\varnothing^\circ$  will be larger and the order is,  $D + W > G + W$ .

Further the plot of  $\varnothing^\circ$  vs  $1/\epsilon_r$ , reciprocal of dielectric constant is found to be linear in all cases and the slope values of these plots are in the order :  $D + W > G + W$  indicating the dependence of  $\varnothing^\circ$  on dielectric constant of the medium and is in agreement with the observation of Gopal *et. al* [4, 5].

**Table 2.**  $S_v / \text{cm}^{9/2}, \text{mol}^{3/2}$ 

|                                   |    | D + W |      |      | G + W |      |      |
|-----------------------------------|----|-------|------|------|-------|------|------|
|                                   |    | 10%   | 20%  | 30%  | 10%   | 20%  | 30%  |
| MgCl <sub>2</sub>                 | 30 | 1.91  | 1.91 | 2.32 | 1.92  | 2.02 | 2.35 |
|                                   | 35 | 1.86  | 1.83 | 2.22 | 1.88  | 1.94 | 2.25 |
|                                   | 40 | 1.88  | 1.87 | 2.42 | 1.90  | 1.98 | 2.29 |
| MgBr <sub>2</sub>                 | 30 | 2.15  | 1.83 | 2.48 | 2.0   | 2.10 | 2.98 |
|                                   | 35 | 2.09  | 1.88 | 2.58 | 2.1   | 2.0  | 2.68 |
|                                   | 40 | 2.11  | 1.94 | 2.68 | 2.2   | 2.07 | 2.78 |
| Mg(NO <sub>3</sub> ) <sub>2</sub> | 30 | 2.18  | 2.10 | 2.55 | 2.3   | 2.42 | 3.02 |
|                                   | 35 | 2.20  | 2.25 | 2.65 | 2.2   | 2.31 | 3.10 |
|                                   | 40 | 2.29  | 2.35 | 2.75 | 2.4   | 2.37 | 3.15 |

**Table 3.**  $\varnothing_{\text{str}}^{\circ} / \text{cm}^3, \text{mole}^{-1}$  at 30°C

| D + W                        |       |       |       |                                    |        |       |       |
|------------------------------|-------|-------|-------|------------------------------------|--------|-------|-------|
|                              | 10%   | 20%   | 30%   | $\varnothing_{\text{int}}^{\circ}$ | 10%    | 20%   | 30%   |
| Cl <sup>-</sup>              | 14.34 | 13.15 | 14.42 | 15.90                              | -0.56  | -2.75 | -1.78 |
| Br <sup>-</sup>              | 15.90 | 12.65 | 25.41 | 20.60                              | -4.70  | -2.95 | 5.41  |
| NO <sub>3</sub> <sup>-</sup> | 20.00 | 21.50 | 24.00 | 25.30                              | -5.30  | -3.50 | -1.30 |
| G + W                        |       |       |       |                                    |        |       |       |
| Cl <sup>-</sup>              | 13.13 | 11.93 | 13.44 | 15.90                              | -1.77  | -3.97 | -1.46 |
| Br <sup>-</sup>              | 13.42 | 14.93 | 22.12 | 28.60                              | -5.77  | 5.67  | 2.38  |
| NO <sub>3</sub> <sup>-</sup> | 14.84 | 16.97 | 24.12 | 25.30                              | -10.46 | -8.33 | -1.18 |

**Table – 4.**  $\Delta V_{\text{tr}}^{\circ}$ 

| D + W                             |     |     |     |     |     |     |
|-----------------------------------|-----|-----|-----|-----|-----|-----|
|                                   | 10% | 20% | 30% | 10% | 20% | 30% |
| MgCl <sub>2</sub>                 | 3.5 | 3.8 | 4.0 | 3.2 | 3.4 | 3.8 |
| MgBr <sub>2</sub>                 | 4.0 | 4.1 | 4.6 | 3.4 | 3.8 | 4.0 |
| Mg(NO <sub>3</sub> ) <sub>2</sub> | 4.5 | 4.9 | 5.1 | 3.9 | 4.4 | 4.8 |

**Limiting Apparent Ionic Volume :**

Attempt has been made to obtain the limited apparent molar volume of Cl<sup>-</sup>, Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in the mixed solvents studied as per the technique suggested by Conway [6]. The plot of  $\varnothing^{\circ}$  vs. molecular weight of anions is almost a straight line. This nearly straight line indicates that the ions are not very much solvated which involves significance electrostriction [8]. By extrapolating the above straight lines to zero molecular weight of the anion the limiting apparent molar volume of Ba<sup>++</sup> is obtained. From this the apparent molar volume of Cl<sup>-</sup>, Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> are determined by making use of the additively law for the apparent molar volume of electrolytes. The volumes of these anions obtained at 30°C are only about structure breaking or making effect,  $\varnothing^{\circ}$  intrinsic of the anions as well as the difference  $\varnothing_{\text{ion}}^{\circ} = \varnothing_{\text{int}}^{\circ}$  are also calculated are given in Table – 3. The instrinsic volume of the anion have been calculated by using the relation,

$$\varnothing_{\text{int}}^{\circ} = 3/4 \pi r^3 N \times 10^{-24} = 2.52 r^3$$

where 'r' is the radius of the ion and N is the Avogadro Number.

From Table 3 it is seen that there is a difference between  $\varnothing_{\text{ion}}^{\circ}$  and  $\varnothing_{\text{int}}^{\circ}$  and it increases with the increase in non-aqueous solvent. So another component  $\varnothing^{\circ}$  structural may be introduced in the expression for  $\varnothing_{\text{ion}}^{\circ}$  to denote the loss or gain in volume of solution. One way is to write, the limiting apparent ionic volume as  $\varnothing_{\text{ion}}^{\circ} = \varnothing_{\text{int}}^{\circ} + \varnothing_{\text{str}}^{\circ}$  in which  $\varnothing_{\text{str}}^{\circ}$  is negative or positive. The negative value is due to the volume contraction and positive volume contraction and positive value is due to volume expansion. The greater the value of  $\varnothing_{\text{str}}^{\circ}$ , the greater is the orderlines and is the ion-solvent interaction and vice-versa. From Table-3 it is seen that ion-solvent interaction is of the order :  $D + W > G + W$ .

#### Volume transfer from $\varnothing^{\circ}$ :

The volumetric behaviour of solutes in solution can provide information concerning solute-solvent and solute-solute interactions. The infinite dilution partial molar volumes are independent of solute-solute interaction and thus can be used to examine solute-solvent interaction. The volume of transfer can be calculated using the equation [7].

$$\Delta V_{\text{tr}}^{\circ} = \varnothing^{\circ} (\text{M.S.}) - \varnothing^{\circ} (\text{W})$$

where  $\varnothing^{\circ}$  (M.S.) is the apparent molar volume at infinite dilution in mixed solvent and  $\varnothing^{\circ}$  is that of water. The  $\Delta V_{\text{tr}}^{\circ}$  at different temperature are recorded in Table-4. The increase in  $\Delta^{\circ}_{\text{t}}$  is due to the decrease in  $\Delta V_{\text{electrostriction}}^{\circ}$  and is less than that of water. So structure breaking effect is more in dioxane + water and less in glycol + water.

This can be explained as follows : dioxane because of its bulky size is not been able to be accommodated in the solvent structure hence it causes a breakdown in the three dimensional water structure. Glycol has got two –OH groups but is not able to break the water structure and is probable due to the low ion-solvent dipole interaction energy. This conclusion has also been drawn from the viscosity and conductivity data.

## ACKNOWLEDGEMENT

**A**uthors are grateful to Dr. P.B. Das, Retd. D.P.I. Orissa, for his valuable advice and encouragement.

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