

Ionic Interaction of MgSO₄ with Mixed Organic Solvents

SYED JUNAID MAHMOOD[†], RAFIA AZMAT^{*}, FAHIM UDDIN[‡] and NOOR TAJ[†]

Department of Chemistry, Jinna University for Women

5C Nazimabad, Karachi-74600, Pakistan

E-mail: rafiasaeed200@yahoo.com

Densities and viscosities (η) of MgSO₄ in formamide and ethylene glycol mixed solvents were measured at three different temperatures. The data was analyzed on the basis of Jones-Dole equation. Positive and increasing values of the B-coefficients show strong solute-solvent or ion-solvent interaction in the given mixed solvent system. Therefore, it may be concluded that the MgSO₄ behaves as structure former or which enhances the structure of 48.32 % mole fraction of formamide + ethylene glycol solvent mixture. This study may be found true in measuring the transition state parameters. The values of free energy of activation of viscous flow of solution ΔU_2° are greater than the values of free energy of activation of viscous flow of solvent system ΔU_1° , which attributes that electrolyte *i.e.* magnesium sulphate is a structure enhancer or maker of the solvent system used in this study. Statistical calculations were also calculated as a function of salt's concentration and temperatures.

Key Words: Magnesium sulphate, Mixed organic solvents, Viscosity, Jones-Dole B equation, Free energy of activation.

INTRODUCTION

A lot of attention and interest has been paid in recent years to electrolyte solutions of mixed solvents in order to analyze the ion-solvent interaction in conjunction with the nature of solvent composition^{1,2}. It was thought that the mixture of formamide and ethylene glycol would be an interesting system. Formamide molecules are self dissociated through intermolecular hydrogen bonding and ethylene glycol molecules are self dissociated through both inter- as well as intra-molecular hydrogen bonding. Due to these interactions it is proved that this solvent system will influence the solvation of ions and interesting results for solute-solvent and solvent-solvent interactions for this mixed solvent system would be found. Another interesting aspect of this study would be that the emphasis would be on 2-2 strong electrolyte (MgSO₄) rather than 1-1 strong electrolyte as solute.

[†]PCSIR Labs Complex Karachi-75280, Pakistan.

[‡]Department of Chemistry, University of Karachi, Karachi-75270, Pakistan.

The viscosity of an electrolyte solution is a very useful quantity for studying ionic solvation. For dilute electrolyte solutions, the relative viscosity (η_r) can be related with salt concentration C , by means of Jones-Dole equation³

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

or

$$\eta_{sp}/C^{1/2} = A + BC^{1/2}$$

where A and B are Jones-Dole coefficients. Ion-ion and ion-solvent interactions of magnesium sulphate in formamide and ethylene glycol mixed solvents were evaluated in terms of A and B coefficients of Jones-Dole equation⁴⁻⁸. The values of A and B coefficients were determined from the intercepts and slopes of the linear plots of η_{sp}/\sqrt{C} versus square root of concentration by least square method. B coefficient in the Jones-Dole equation represents the ion-solvent interactions and is the measure of the interaction of the added electrolyte in a particular medium⁵⁻⁹. Values of B coefficient can be obtained by the slope of the plot of η_{sp}/\sqrt{C} versus square root of concentration. B coefficient is a highly specific property of solute concerned with additive of ionic concentration to the viscosity¹⁰⁻¹⁵. The B -coefficient can be discussed in terms of factors affecting the viscosity at a particular concentration of salt and temperature. The B -coefficient is an empirical constant, which is a measure of ion-solvent interactions. This can have positive and negative values.

In the present work, the B -coefficient of $MgSO_4$ in formamide and ethylene glycol mixture have been determined at 298.14, 303 and 308 K by using density (ρ) and viscosity (η) data. The study plan was further extended to evaluate the transition parameters such as free energy of activation of viscous flow.

EXPERIMENTAL

Formamide (Merck of analytical grade), was dried over molecular sieves (4A) and then neutralized with NaOH pellets and distilled water. Formamide solution was stored in sealed container in the dark cold room.

Ethylene glycol (BDH) was dried over molecular sieves (4A) for several days. The binary solvent mixture of 48.32 % mole fraction of formamide in ethylene glycol was prepared by volume. The mixture was kept in tightly sealed bottle to minimize absorption of moisture and CO_2 from the atmosphere⁷. $MgSO_4 \cdot 7H_2O$ (BDH) was used after being dried over P_2O_5 . Mixtures of $MgSO_4$ with 48.32 % mole fraction of formamide were prepared ranging from 0.0195 to 0.195 M. The weighing was done by Libror Eb-3200/t digital balance with a precision of ± 0.001 mg. Densities of pure formamide, mixture of formamide with ethylene glycol and solutions of $MgSO_4$ in pure formamide as well as in 48.32 % mole fraction of formamide were measured with the help of relative density bottle having a capacity of 20 mL at three different temperatures. Temperature was kept constant by keeping the solution in

thermostatic bath for at least 15 min to attain the equilibrium. Viscosity measurements were carried out by using an Ubbelohde suspended level viscometer* with the flow time of 200 s for distilled water at 298.13 K.

The viscometer was calibrated by the method described by Gill and Sharma⁸. The viscometer was suspended in the water thermostat bath whose temperature was maintained at 298.13 ± 0.01 K. The re-reducibility of the viscosity measurements was found to be ± 0.002cP.

RESULTS AND DISCUSSION

The measured densities (ρ) and viscosities (η) of solvent mixtures and solutions of MgSO₄ within the concentration range (0.012-0.20) mol dm⁻³ at 298, 303 and 308 K are tabulated in Table-1. The empirical Jones-Dole equation for relative viscosity was fitted to viscosity data to evaluate A and B coefficients by least squares,

$$\eta_r = \eta/\eta_0 = 1 + AC^{1/2} + BC \quad (1)$$

TABLE-1
DENSITY AND VISCOSITY OF MgSO₄ IN FORMAMIDE AND ETHYLENE GLYCOL MIXTURE AT 298, 303 AND 308 K

| C (mol dm ⁻³) | Density, ρ (Kg m ⁻³) | Viscosity, η (10 ⁻³ N m ⁻² s) |
|---------------------------|---------------------------------------|--|
| At 298 K | | |
| Pure mixture | 1116.31 | 7.1154 |
| 0.0101 | 1116.70 | 7.2113 |
| 0.0496 | 1121.39 | 7.6932 |
| 0.1002 | 1126.38 | 8.3668 |
| 0.1510 | 1131.71 | 9.2679 |
| 0.2010 | 1136.89 | 10.0932 |
| At 303 K | | |
| 0.0101 | 1115.20 | 7.1151 |
| 0.0496 | 1118.79 | 7.2101 |
| 0.1002 | 1123.50 | 7.6399 |
| 0.1510 | 1128.49 | 9.2109 |
| 0.2010 | 1131.90 | 10.0054 |
| At 308 K | | |
| 0.0101 | 1089.49 | 7.1109 |
| 0.0496 | 1109.89 | 7.2074 |
| 0.1002 | 1115.39 | 7.4377 |
| 0.1510 | 1119.89 | 8.8998 |
| 0.2010 | 1125.69 | 9.9016 |

In equation 1, η and η_0 are viscosities of the solutions and solvents, respectively. C is the molar concentration of electrolyte. A and B are constants¹⁶. The A coefficient accounts for an ionic atmosphere conditions and B-coefficient is related to the effect of ion size on the viscosity.

*Techniconomial Constant 0.1 cS/S Capillary ASTM D445.

So the rearrangement of eqn. 1 produces

$$\frac{\eta - \eta_0}{\eta_0 C^{1/2}} = A + BC^{1/2} \quad (2)$$

The values of A and B coefficients were determined from the intercepts and slopes of the linear plots of η_{sp}/\sqrt{C} versus square root of concentration by least square method. Representative plots of η_{sp}/\sqrt{C} against square root of concentration for magnesium sulphate (MgSO_4) in ethylene glycol and formamide mixtures at 298 K temperatures are shown in Fig. 1. The values of viscosities A and B-coefficients are tabulated in Table-2. It is observed from the values tabulated in Table-2 that the values of viscosity A-coefficients are very small at all the three temperatures. The small A-coefficients values indicate the weak ion-ion interactions in the said solvent system. The viscosity A-coefficients at all the three temperatures have negative values and such results are probably with out physical significance⁷. The lower and negative values of A coefficient with rise in temperature in formamide and ethylene glycol mixed solvents show that more violent thermal agitation at higher temperature results in reduction of attractive forces. However, interpenetration effect of (cation-cation) and (cation-anion) also brings ions together. This may be responsible for the increase in negative

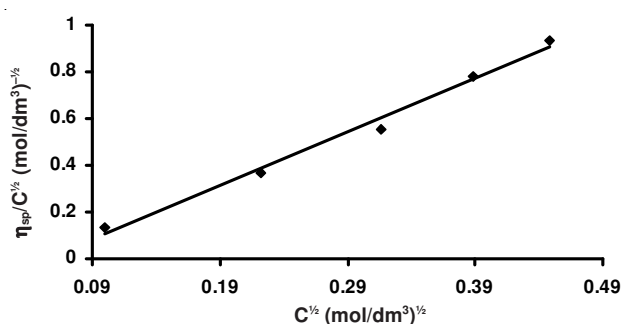


Fig. 1. Plot of $\eta_{sp}/C^{1/2}$ vs. square root of concentration of magnesium sulphate in formamide and ethylene glycol solution at 298 K

TABLE-2
VALUES OF VISCOSITY A-COEFFICIENTS AND B-COEFFICIENTS FOR
 MgSO_4 in 48.32 % MOLE FRACTION OF FORMAMIDE + ETHYLENE
GLYCOL MIXTURE AT THREE DIFFERENT TEMPERATURES

| Temperature (K) | A ($\text{dm}^{3/2} \text{ mol}^{-1/2}$) | B ($\text{dm}^3 \text{ mol}^{-1}$) |
|-----------------|--|--------------------------------------|
| 298 | -0.1312 ± 0.001 | 2.325 ± 0.0009 |
| 303 | -0.4274 ± 0.004 | 2.779 ± 0.0001 |
| 308 | -0.4015 ± 0.003 | 2.535 ± 0.0004 |

values of coefficient 'A'. Some variations observed in A coefficient may be attributed to the size of ions which differ in degrees of hydration. The negative values of the A coefficient show that formamide and ethylene glycol mixed solvents association to water is stronger as compared to the solvent interactions with ions.

A similar difficulty was encountered by Kay *et al.*⁹. These workers related the errors to a surface tension effect resulting from very small traces of surface-active impurities in the salt.

The B-coefficients of MgSO₄ studied at different temperatures are reported in Table-2. The magnitude of the B-coefficients is determined by the ion size and by ion-solvent and solvent-solvent interaction. The B-coefficients of MgSO₄ at all the three temperatures are positive. This may be attributed to strong ion-solvent interaction in the system and shows the structure making effect of the electrolyte, which is a common feature of most non-aqueous solvents¹⁰. This is also observed that the values of B-coefficients were increased with the increase in temperature. This may be attributed to strong ion-solvent interaction and the structure making ability of MgSO₄¹¹. The viscosity data (Table-1) for magnesium sulphate in formamide and ethylene glycol mixtures systems have found to be decreased with the increase in temperature, which means that the flow rate of MgSO₄ in 48.32 % mole fraction of formamide + ethylene glycol solvent mixture was increased with the increase in temperature¹². The measured values of the densities and viscosities were also used to calculate the apparent molar volumes (ϕ_v) of MgSO₄·7H₂O in mixed solvents by using the following relation.

$$\phi_v = \frac{1000(\rho_0 - \rho)}{C\rho_0} + \frac{M}{\rho_0} \quad (3)$$

where ρ_0 and ρ are densities of solvent mixture and solution respectively. M is the molecular weight of the electrolyte used while C is the concentration of magnesium sulphate¹⁷⁻¹⁹. The partial molar volumes ($\phi_v = V_o$) at infinite dilution were determined by using least square method and fit to the plots of ϕ_v versus $C^{1/2}$ in accordance with Masson's empirical relation¹³.

$$\phi_v = \phi_v^0 + S_v C^{1/2} \quad (4)$$

The calculated values of intercept (ϕ_v^0) and slope (S_v) at 298, 303 and 308 K of magnesium sulphate in mixed solvent system *i.e.* formamide and ethylene glycol are given in Table-3. ϕ_v^0 is a measure of ion solvent interaction. It is evident from the Table-3 that ϕ_v^0 values are large and positive for MgSO₄ in formamide + ethylene glycol mixture suggesting the presence of strong ion solvent interactions. Increase in the values of ϕ_v^0 on increasing the temperature from 298 to 308 K indicates the increasing trend of the ion solvent interaction as the temperature of the solution increases. Representative

plots of apparent molar volumes (ϕ_v) against square root of concentration for MgSO_4 in ethylene glycol and formamide mixtures at 298 K temperatures are shown in Fig. 2.

TABLE-3
PARTIAL MOLAR VOLUMES (ϕ_v°) AND SLOPE (S_v) OF MgSO_4 IN 48.32 %
MOLE FRACTION OF FORMAMIDE + ETHYLENE GLYCOL MIXTURE
AT THREE DIFFERENT TEMPERATURES

| Temperature (K) | ϕ_v° ($\text{m}^3 \text{mol}^{-1}$) | S_v ($\text{dm}^{3/2} \text{mol}^{-3/2}$) |
|-----------------|---|---|
| 298 | -0.0037 | -0.0146 |
| 303 | 0.0105 | -0.0459 |
| 308 | 0.2389 | -0.6435 |

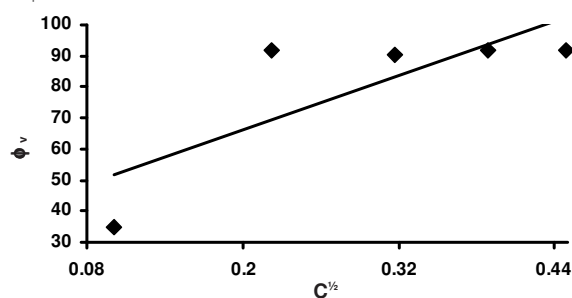


Fig. 2. Plot of ϕ_v vs. square root of concentration of magnesium sulphate in formamide and ethylene glycol solution at 298 K

The value of slope (S_v) measures the ion-ion interaction and depends on charge, salt type and nature of salt. The values of S_v was found to be negative at given temperatures indicating the presence of weak ion-ion interaction. In fact, negative S_v values are the function of the solvents of high dielectric constant¹⁴. Literature surveyed¹⁵ reveals that formamide and ethylene glycol have a high dielectric constant 111.0 and 37.7, respectively at 298 K and it is also observed from the literature that the values of S_v are negative for the electrolytes in high dielectric constant media such as water and water formic acid mixtures¹⁶. This is attributed to the fact that in solvent of high dielectric constant like formamide and ethylene glycol the salts remain completely ionized even at fairly high concentrations and resulting to negative values of slope for the plot¹⁷ of apparent molar volumes (ϕ_v) vs. $C^{1/2}$.

Moreover, the thermodynamic parameter such as free energy of activation of viscous flow of solvent (ΔU_1°) and free energy of activation of viscous flow of solution (ΔU_2°) was calculated by using the transition state theory of relative viscosity of electrolyte solution proposed by Feakins *et al.*¹⁷.

$$B = (\bar{V}_1^0 - \bar{V}_2^0)/1000 + \bar{V}_1^0(\Delta\mu_2^0 - \Delta\mu_1^0)/RT/1000 \quad (5)$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of the solvent and solute, respectively. $\Delta\mu_2^0$ is the contribution per mole of solute to the free energy of activation of viscous flow of the solution and $\Delta\mu_1^0$ is the free energy of the activation per mole of the pure solvent. $\Delta\mu_2^0$ is calculated using the following equation.

$$\Delta G_1 = \Delta\mu_1^0 = RT \ln (\eta_0 V_1^0/hN) \quad (6)$$

$$\Delta G_2 = \Delta\mu_2^0 = \Delta\mu_1^0 + (RT/V_1^0)[1000 B - (V_1^0 - V_2^0)] \quad (7)$$

where R = gas constant, h = Planck's constant, N = Avogadro's number and T = absolute temperature. It is clear from the Table-4 that $\Delta\mu_2^0$ values are very large as compared to the values of $\Delta\mu_1^0$ which are attributed to the strong ion-solvent interaction for MgSO₄ in formamide and ethylene glycol mixtures as compared to the pure mixtures *i.e.* formamide and ethylene glycol. Moreover, $\Delta\mu_2^0$ tends to increase with increasing the temperature of the solution¹⁹. It may also be noted that the values of free energy of activation of viscous flow of pure solvent ($\Delta\mu_1^0$) of MgSO₄ in mixed solvent system at given temperatures is greater than zero and this is due to the fact that MgSO₄ in formamide + ethylene glycol mixed solvent behaves as a structure maker. This theory is also explained by Feakins *et al.*¹⁷ that if $\Delta\mu_2^0 > \Delta\mu_1^0$ for electrolytes, then those electrolytes behave as structure makers.

TABLE-4
VALUES OF FREE ENERGY OF ACTIVATION FOR THE SOLVENT $\Delta\mu_1^0$
AND SOLVENT $\Delta\mu_2^0$ IN 40 % FORMAMIDE + ETHYLENE GLYCOL
AT VARIOUS TEMPERATURES

| Temperature (K) | $\Delta\mu_1^0$ (kJ mol ⁻¹) | $\Delta\mu_2^0$ (kJ mol ⁻¹) |
|-----------------|---|---|
| 298 | 11.99 ± 0.001 | 105.31 ± 0.0004 |
| 303 | 14.59 ± 0.004 | 131.93 ± 0.0005 |
| 308 | 16.81 ± 0.003 | 140.01 ± 0.0004 |

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