

Density and viscosity of magnesium sulphate in formamide + ethylene glycol mixed solvents

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MS received 15 March 2002; revised 4 July 2002

Abstract. Densities (ρ) and viscosities (η) of different strengths of magnesium sulphate (MgSO_4) in varying proportions of formamide (FA) + ethylene glycol as mixed solvents were measured at room temperature. The experimental values of ρ and η were used to calculate the values of the apparent molar volume, (ϕ_v), partial molar volume, (ϕ_v°) at infinite dilution, A - and B -coefficients of the Jones–Dole equation and free energies of activation of viscous flow, ($\Delta\mu_1^{0*}$) and ($\Delta\mu_2^{0*}$), per mole of solvent and solute respectively. The behaviour of these parameters suggests strong ion–solvent interactions in these systems and also that MgSO_4 acts as structure-maker in FA + ethylene glycol mixed solvents.

Keywords. Magnesium sulphate; formamide–ethylene glycol mixture; activation energy of viscous flow.

1. Introduction

Studies on the behaviour of ions in mixed water + non-aqueous solvents have received a lot of attention in the recent past^{1–3}. However, similar studies of electrolytes in non-aqueous binary solvents are scarce in the literature. Precise data on electrolytes in mixed solvents find applications in many industrial processes, as they provide a wide choice of solutions with appropriate properties. An attempt has been made to investigate the ion–solvent interactions of magnesium sulphate (MgSO_4) in formamide (FA) and ethylene glycol mixtures. In the pure liquid, FA molecules are self-associated through inter-molecular H-bonding, while those of ethylene glycol molecules are self-associated through inter- as well as intra-molecular hydrogen bonding⁴. It is found that the character of the molecular interaction considerably influences the solvation of ions. Thus, FA + ethylene glycol mixed solvents would be interesting media for the study of ion–solvent and solvent–solvent interactions of MgSO_4 .

In the present study, the density (ρ) and viscosity (η) of MgSO_4 (0.01, 0.05, 0.10, 0.15 and 0.20 molar (M) solutions) in 20, 40 and 60% (v/v) FA + ethylene glycol mixtures have been measured at 298 K. Experimental values of ρ and η were used to calculate the apparent molar volume (ϕ_v), limiting (infinite dilution) apparent molar volume (also called partial molar volume) (ϕ_v°), A - and B -coefficients of the Jones–Dole⁵ equation, and the free energies of activation of viscous flow ($\Delta\mu_1^{0*}$) and ($\Delta\mu_2^{0*}$) per mole of

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solvent and solute respectively, in all the three solvent mixtures. These parameters are the true representatives of the behaviour of ions in a given solution.

2. Experimental

Formamide used was the same as in our recent study⁶. Ethylene glycol (s.d. Fine, India) of AR grade was purified as described in the literature⁷. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, also of same make and grade, was used without further purification, except for being dried over P_2O_5 . The binary solvent mixtures of 20, 40 and 60% FA + ethylene glycol were prepared by volume. Mixtures of 0.01, 0.05, 0.10, 0.15 and 0.20 M – MgSO_4 in all the three FA + ethylene glycol solvents were prepared in a dry atmosphere. All the solutions were kept tightly sealed to minimize absorption of atmospheric moisture and carbon dioxide. The weighings were done on an Afcoset ER-120A electronic balance with a precision of ± 0.1 mg. Densities of the mixed solvents and those of the solutions of MgSO_4 in these solvents were measured with the help of a single-stem pycnometer of bulb capacity $8 \times 10^{-3} \text{ dm}^3$ with graduated marks on the stem. The neck of the stem could be closed with a well-fitting glass cap. The marks on the stem were calibrated using double-distilled water. Viscosities were determined using an Ubbelohde type⁸ viscometer. The temperature of the solutions was maintained at 298 ± 0.05 K in an electronically controlled thermostatic water bath. The accuracies in density and viscosity measurements were found to be $\pm 0.01 \text{ kg m}^{-3}$ and $\pm 3 \times 10^{-6} \text{ Nm}^{-2} \text{ s}$ respectively.

3. Results and discussion

Measured densities and viscosities of 0.01, 0.05, 0.10, 0.15 and 0.20 M – MgSO_4 in 20, 40 and 60% (v/v) FA + ethylene glycol solvents at 298 K are listed in table 1. These experimental values of ρ and η were used to calculate the apparent molar volumes (ϕ_v) of MgSO_4 in mixed solvents using the following relation,

$$\phi_v = 1000(\rho_0 - \rho)/C\rho_0 + M_2/\rho_0, \quad (1)$$

where ρ_0 and ρ are the densities of the solvent and solution, respectively; C is the molar concentration of electrolyte and M_2 is its molecular weight. The apparent molar volume (ϕ_v) was found to vary linearly with the square root of the concentration of the electrolyte. Hence, the partial molar volumes (ϕ_v°) ($=\bar{V}^0$) at infinite dilution were calculated by the method of least squares and fit to the plots of ϕ_v versus $C^{1/2}$ in accordance with Masson's empirical relation⁹,

$$\phi_v = \phi_v^\circ + S_v^* C^{1/2}. \quad (2)$$

The calculated values of ϕ_v° and S_v^* , intercept and slope, of ϕ_v versus $C^{1/2}$ plots in 20, 40 and 60% (v/v) FA + ethylene glycol mixed solvents at 298 K are given in table 2. S_v^* is a measure of ion-ion interaction and depends on charge, salt-type and nature of the solvent. Table 2 shows that all the values of S_v^* are large and negative indicating the presence of weak ion-ion interactions in the solution. Moreover, the values of S_v^* become less negative with increase in FA content in the system, suggesting increased ion-ion interaction in the FA-rich solvent. In fact, negative S_v^* values are often obtained in solvents of high dielectric constant¹⁰, as FA + ethylene glycol mixed solvents in the

Table 1. Values of density (ρ) and viscosity (η) of $MgSO_4$ + FA + ethylene glycol solutions as function of molar concentration (C) of $MgSO_4$ and volume (%) of FA at 298 K.

C (molar)	ρ ($kg\ m^{-3}$)	η ($10^{-3}\ Nm^{-2}\ s$)
<i>20% FA + ethylene glycol</i>		
0.00	1114.1	10.6058
0.01	1114.5	10.7259
0.05	1118.7	11.4607
0.10	1124.7	12.6732
0.15	1129.6	13.7242
0.20	1134.9	14.6458
<i>40% FA + ethylene glycol</i>		
0.00	1116.3	7.1155
0.01	1116.7	7.2113
0.05	1121.4	7.6932
0.10	1126.4	8.3668
0.15	1131.7	9.2680
0.20	1136.9	10.0993
<i>60% FA + ethylene glycol</i>		
0.00	1130.9	5.1838
0.01	1121.4	5.3008
0.05	1125.5	5.6865
0.10	1131.5	6.3094
0.15	1136.6	7.1299
0.20	1142.1	8.0140

Table 2. Values of partial molar volume (ϕ_v°) and experimental slope (S_v^*) of $MgSO_4$ in FA + ethylene glycol mixtures at infinite dilution, using Masson's empirical equation, at 298 K.

Volume (%) of FA in (FA + ethylene glycol)	ϕ_v° ($10^{-4}\ m^3\ mol^{-1}$)	S_v^* ($10^{-4}\ m^3\ dm^{3/2}\ mol^{-3/2}$)
20	1.8808	-1.3974
40	1.8349	-1.4610
60	1.7925	-1.5872

present study, which are expected to have high dielectric constants since both the liquids FA and ethylene glycol have high dielectric constants 111.0 and 37.7¹¹, respectively, at 298 K. Negative values of S_v^* for electrolytes in high dielectric constant media (water and water + formic acid mixtures) have also been reported¹². This is attributed to the fact that in solvents of high dielectric constant, like FA + ethylene glycol, the salts remain completely ionized, even at fairly high concentrations. As a result, appreciable interionic penetration is likely to occur, giving rise to negative slope for ϕ_v versus $C^{1/2}$ plots¹.

ϕ_v° is regarded as a measure of ion–solvent interaction. It is evident from table 2 that ϕ_v° values are large positive for $MgSO_4$ in FA + ethylene glycol mixtures, suggesting the

presence of strong ion–solvent interactions. Small decrease in ϕ_v° on going from 20 to 60% FA indicates the decreasing trend of the ion–solvent interaction as the amount of FA in the solution increases. This, in turn, supports the behaviour of S_v^* which predicts increased ion–ion interaction as the content of FA in the solution increases. This is contrary to our expectation, as the calculated dielectric constant of FA + ethylene glycol mixtures would increase with increasing amount of FA (with higher dielectric constant) in these mixtures. The dielectric constants of the present mixtures can be calculated using the procedure adopted by Rohdewald and Moldner¹³. These authors calculated the dielectric constants for a binary and ternary or even for higher liquid mixtures using the formula,

$$\epsilon_{\text{mix}} = [(\% \text{ solvent}_1) \epsilon_1 + (\% \text{ solvent}_2) \epsilon_2 + \dots + (\% \text{ solvent}_i) \epsilon_i] / 100. \quad (3)$$

The calculated values of dielectric constants for 20, 40 and 60% FA + ethylene glycol mixtures are found to be 52.36, 67.02 and 81.68 at 298 K. As a result, due to increase in dielectric constant, ion–solvent interaction should increase on going from 20 to 60% FA in these solutions. However, the observed trend in ϕ_v° (table 2) suggests the reverse. We thus anticipate that solvent–solvent interaction through hydrogen-bonding between FA and ethylene glycol molecules seems to be sufficiently strong to prevent (the expected) increase in ion–solvent interaction as the amount of FA in the solution increases on going from 20 to 60% FA.

The viscosity data of the present solutions were analysed by using the Jones–Dole⁵ equation,

$$\eta_r = \eta / \eta_0 = 1 + AC^{1/2} + BC, \quad (4)$$

where η and η_0 , respectively, are the dynamic viscosities of solution and solvent, η_r is the relative viscosity of the solution, A is the Falkenhagen coefficient¹⁴ and is a measure of ion–ion interactions theoretically. On the other hand, B , the Jones–Dole coefficient, is empirical and is a function of the ion–solvent interactions. The coefficients A and B were calculated by least-squares fitting of the experimental η values in the Jones–Dole equation (4). The values of A and B thus obtained are listed in table 3. It is observed that the values of A -coefficients are very small in all the three solvent mixtures. This indicates the presence of weak ion–ion interactions in the system studied. A perusal of table 3 suggests that the B -coefficients for MgSO_4 in all the three solvent mixtures are quite positive. This may be attributed to strong ion–solvent interaction in the system.

Furthermore, the viscosity data were also examined in the light of the transition state theory of the relative viscosity of electrolyte solutions proposed by Feakins *et al*¹⁵. According to the theory, B -coefficient is given as,

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

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 activation per mole of the pure solvent. The values of $\Delta\mu_1^{0*}$ ¹⁶ and thereafter those of $\Delta\mu_2^{0*}$ were calculated using the following equations.

Table 3. Values of A - and B -coefficients of Jones–Dole equation for $MgSO_4$ in FA + ethylene glycol mixtures at 298 K.

Volume (%) of FA in (FA + ethylene glycol)	A ($dm^{3/2} mol^{-1/2}$)	B ($dm^3 mol^{-1}$)
20	-0.1076	2.1970
40	-0.1305	2.3229
60	-0.1366	2.8616

Table 4. Values of free energy of activation for the solvent ($\Delta\mu_1^{0*}$) and solute ($\Delta\mu_2^{0*}$) in FA + ethylene mixtures at 298 K.

Volume (%) of FA in (FA + ethylene glycol)	$\Delta\mu_1^{0*}$ ($kJ mol^{-1}$)	$\Delta\mu_2^{0*}$ ($kJ mol^{-1}$)
20	17.95	118.98
40	16.81	140.01
60	15.86	176.55

$$\Delta\mu_1^{0*} = RT \ln(\eta_0 \bar{V}^0 / hN), \quad (6)$$

and

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + (RT / \bar{V}^0)[1000B - (\bar{V}_1^0 - \bar{V}_2^0)], \quad (7)$$

where R , h and N are gas constant, Planck's constant and Avogadro's constant respectively, and T is the absolute temperature. The calculated values of $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ are given in table 4. It is clear from table 4 that $\Delta\mu_2^{0*}$ values are very large as compared to those of $\Delta\mu_1^{0*}$ in all the three electrolyte + solvent mixtures. Moreover, $\Delta\mu_2^{0*}$ tends to increase with increasing amount of FA in the solution. This suggests that the process of viscous flow becomes difficult as the content of FA in the solution increases. This may be attributed to the strong ion–solvent interaction in the solution. Thus, the behaviour of $\Delta\mu_2^{0*}$ reinforces our earlier contention that strong ion–solvent interaction exists in the present $MgSO_4$ + mixed solvent systems. It may be noted that for all the $MgSO_4$ + mixed solvent systems ($\Delta\mu_2^{0*} - \Delta\mu_1^{0*}$) > 0. This is due to the fact that $MgSO_4$ in FA + ethylene glycol mixed solvent behaves as structure-maker. In fact, Feakins *et al*¹⁵ have shown that $\Delta\mu_2^{0*} > \Delta\mu_1^{0*}$ for electrolytes that are structure-makers. A similar conclusion regarding $MgSO_4$ in dioxane + water mixed solvents were also arrived at by Kannappan and Rajendran¹⁷ from ultrasonic studies of the above solutions.

Acknowledgements

The authors (AA, AKN and NK) thank the Department of Science and Technology, Council of Scientific Industrial Research and University Grants Commission, New Delhi for financial support for the project, and Research Associateship and Teacher Fellowship respectively.

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