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Apparent Molar Volumes and Viscosity B-Coefficients of Glycine in Aqueous Silver Sulphate Solutions at $T = (298.15, 308.15, 318.15)$ K

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Abstract

Apparent molar volumes (φ_v) and viscosity B -coefficients for glycine in 0.005, 0.010, 0.015, and 0.020 mol.dm⁻³ aqueous silver sulphate (Ag₂SO₄) solutions have been determined from solution density and viscosity measurements at (298.15, 308.15, and 318.15) K as a function of glycine concentration. The standard partial molar volume (φ_v^0) and experimental slopes (S_v^*) obtained from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data were analyzed using the Jones-Dole equation, and the derived parameters A and B were interpreted in terms of solute-solute and solute-solvent interactions, respectively. The standard volumes of transfer ($\Delta\varphi_v^0$) and viscosity B -coefficients of transfer (ΔB) of glycine from water to aqueous Ag₂SO₄ solutions were derived to study various interactions in the ternary solutions. The structure making or breaking ability of glycine has been discussed in terms of the sign of $(\delta^2\varphi_v^0/\delta T^2)_p$. The activation parameters of viscous flow for the ternary solutions were also calculated and explained in terms of transition state theory.

Keywords: Density, Viscosity, Partial molar volume, Viscosity B -coefficient, Glycine, Aqueous silver sulphate solutions.

1. Introduction

Amino acids and peptides are the fundamental structural units of proteins and thermodynamic properties of these model compounds in aqueous medium provide information about solute-solvent and solute-solute interactions that help us to understand several biochemical processes such as protein hydration, denaturation, aggregation etc.¹⁻⁴ It has been found that salt solutions have large effects on the structure and the properties of proteins including their solubility, denaturation, dissociation into subunits, and the activity of enzymes.^{5,6} Proteins are complex molecules, and their behavior in solution is governed by a combination of many specific interactions. One approach that reduces the degree of complexity and requires less complex measurement techniques is to study the interaction in systems containing smaller bio-molecules, such as amino acids and pep-

tides. Many cations and anions of neutral salts affect the properties of proteins such as their solubility, stability and biological activity in widely different manner.^{5,6} It is well established that various co-solutes, co-solvents such as guanidine hydrochloride,^{7,8} potassium thiocyanate,⁹ potassium chloride,¹⁰ tetraalkylammonium salts,^{11,12} can act as effective probes of their conformation in solutions.¹³⁻¹⁶

Thermodynamic properties of amino acids in aqueous electrolyte solution thus provide valuable information about solute-solvent and solute-solute interactions. Hence there has been a number of works^{7-12,21,32} revealing the effect of electrolytic solutions on amino acids. But to the best of our knowledge such studies in aqueous Ag₂SO₄ solutions are rare in the literature. Hence in this paper, an attempt has been made to unravel the various interactions in the ternary systems of glycine + Ag₂SO₄ + water at 298.15, 308.15 and 318.15 K.

2. Experimental

2. 1. Materials

Glycine (Analar, BDH, purity >99%), and silver sulphate (Ag_2SO_4) were used for the present study. Glycine was purified by re-crystallizing from methanol-water mixture and dried at 373.15 K for 12 h in an infrared drier and then in vacuo over P_2O_5 at room temperature. Ag_2SO_4 (Loba Chemie, India, purity > 98.5%) was recrystallized from concentrated sulfuric acid, cooled, then diluted with de-ionized water and the precipitate was filtered, washed and dried at 120 °C.

De-ionized, doubly distilled, degassed water with a specific conductance $< 10^{-6} \text{ S cm}^{-1}$ was used for the preparation of different aqueous Ag_2SO_4 solutions. The physical properties of different aqueous Ag_2SO_4 solutions are listed in Table 1.

Table 1: Densities and viscosities of different aqueous Ag_2SO_4 solutions at different temperatures.

| Molarity of Ag_2SO_4 in Aqueous solution | T (K) | $\rho \times 10^{-3}$ (kg m^{-3}) | η (mPa s) |
|--|---------|--|----------------|
| 0.005 mol dm^{-3} | 298.15 | 0.9990 | 0.751 |
| | 308.15 | 0.9956 | 0.614 |
| | 318.15 | 0.9907 | 0.502 |
| 0.010 mol dm^{-3} | 298.15 | 1.0005 | 0.817 |
| | 308.15 | 0.9973 | 0.725 |
| | 318.15 | 0.9930 | 0.567 |
| 0.015 mol dm^{-3} | 298.15 | 1.0021 | 0.842 |
| | 308.15 | 0.9988 | 0.715 |
| | 318.15 | 0.9940 | 0.577 |
| 0.020 mol dm^{-3} | 298.15 | 1.0035 | 0.821 |
| | 308.15 | 1.0000 | 0.693 |
| | 318.15 | 0.9965 | 0.609 |

2. 2. Preparation of solutions

Stock solutions of glycine in different aqueous Ag_2SO_4 solutions were prepared by mass and the working solutions were prepared by mass dilution. The conversion of molality into molarity was accomplished using the experimental density values. The uncertainty of molarity of the glycine solutions is evaluated to be $\pm 0.0001 \text{ mol dm}^{-3}$.

2. 3. Density Measurements

The densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of about 0.1 cm. The pycnometer was calibrated at the experimental temperatures with doubly distilled water and purified methanol. The pycnometer with experimental liquid was equilibrated in a glass-walled thermostated water bath maintained at ± 0.01

K of the desired temperature. The pycnometer was then removed from the thermostat bath, properly dried and weighed. The mass measurements were done on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with a precision of $\pm 0.01 \text{ mg}$. Adequate precautions were taken to avoid evaporation losses during the actual measurements. An average of triplicate measurement was taken into account. The precision of density measurements was evaluated to be within $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$.

2. 3. Viscosity Measurements

The viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at the experimental temperatures with doubly distilled water and purified methanol. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed vertically in a glass-walled thermostat maintained to $\pm 0.01 \text{ K}$. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch correct to $\pm 0.1 \text{ s}$. At least three repetition of each data reproducible to $\pm 0.1 \text{ s}$ were taken to average the flow time. The uncertainty in viscosity measurements is within $\pm 0.003 \text{ mPa s}$. Details of the methods and techniques of the density and viscosity measurements have been described elsewhere.^{17–19}

3. Results and Discussion

Experimental values of molarity (c), densities (ρ), viscosities (η), and derived parameters at (298.15, 308.15, 318.15) K are listed in Table 2.

3. 1. Apparent Molar Volumes

The apparent molar volumes (ϕ_V) were determined from the solution densities using the following equation:¹²

$$\phi_V = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (1)$$

where M is the molar mass of the solute, c is the molarity of the glycine in Ag_2SO_4 + water mixtures, ρ_0 and ρ are the densities of the solvent and the solution respectively. As the plots of ϕ_V values against square root of molar concentrations (\sqrt{c}) were linear, ϕ_V values were fitted to the Massion equation:²⁰

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c} \quad (2)$$

where ϕ_V^0 is the partial molar volume at infinite dilution and S_V^* is the experimental slope. The ϕ_V^0 values have been determined by fitting the dilute data ($c < 0.1$) to Eq. (2) using a weighted least square fit. Values of ϕ_V^0 and S_V^* along with the corresponding standard deviation (σ) are listed in Table 3. The estimated uncertainties in ϕ_V^0 are equal to

standard deviation (σ), the root mean square of the deviation between the experimental and calculated φ_V^0 for each data point. The φ_V^0 and S_V^* values for glycine in pure water were obtained from the literature^{21,22} and were used in subsequent calculations.

Table 3 shows that φ_V^0 values are positive and increase with a rise in the molarity of Ag_2SO_4 in the mix-

ture, but decrease as the temperature of the respective mixture increases. This indicates the presence of strong solute-solvent interactions and these interactions are further strengthened at higher molarity of Ag_2SO_4 in the solutions but decreases at higher temperatures probably due to more thermal agitations at higher temperatures.

Table 2: Molarities, densities, viscosities, apparent molar volumes and $(\eta_r - 1)/\sqrt{c}$ for glycine in different aqueous Ag_2SO_4 solutions at different temperatures.

| c (mol dm ⁻³) | $\rho \times 10^{-3}$ (kg m ⁻³) | η (mPa s) | $\varphi \times 10^6$ (m ⁻³ mol ⁻¹) | $\frac{(\eta_r - 1)}{\sqrt{c}}$ |
|--|--|-------------------|---|---------------------------------|
| 0.005 mol dm ⁻³ of Ag_2SO_4 in aqueous solution | | | | |
| $T = 298.15$ K | | | | |
| 0.0239 | 0.9998 | 0.757 | 41.37 | 0.0540 |
| 0.0320 | 1.0001 | 0.759 | 41.90 | 0.0622 |
| 0.0560 | 1.0008 | 0.764 | 43.18 | 0.0714 |
| 0.0720 | 1.0012 | 0.768 | 43.90 | 0.0836 |
| 0.0880 | 1.0017 | 0.772 | 44.20 | 0.0942 |
| 0.0999 | 1.0020 | 0.776 | 44.60 | 0.1030 |
| $T = 308.15$ K | | | | |
| 0.0239 | 0.9965 | 0.625 | 39.24 | 0.1149 |
| 0.0319 | 0.9967 | 0.628 | 39.76 | 0.1200 |
| 0.0558 | 0.9975 | 0.635 | 41.97 | 0.1420 |
| 0.0718 | 0.9979 | 0.638 | 42.58 | 0.1439 |
| 0.0877 | 0.9984 | 0.642 | 43.66 | 0.1530 |
| 0.0996 | 0.9987 | 0.644 | 43.89 | 0.1520 |
| $T = 318.15$ K | | | | |
| 0.0238 | 0.9918 | 0.512 | 26.99 | 0.1303 |
| 0.0318 | 0.9922 | 0.513 | 28.50 | 0.1320 |
| 0.0556 | 0.9932 | 0.518 | 30.42 | 0.1410 |
| 0.0715 | 0.9939 | 0.521 | 31.06 | 0.1420 |
| 0.0873 | 0.9945 | 0.523 | 32.19 | 0.1470 |
| 0.0992 | 0.9948 | 0.525 | 34.00 | 0.1464 |
| 0.010 mol dm ⁻³ of Ag_2SO_4 in aqueous solution | | | | |
| $T = 298.15$ K | | | | |
| 0.0240 | 1.0013 | 0.827 | 42.59 | 0.0799 |
| 0.0320 | 1.0015 | 0.829 | 42.90 | 0.0850 |
| 0.0560 | 1.0022 | 0.838 | 43.79 | 0.1099 |
| 0.0720 | 1.0027 | 0.845 | 44.18 | 0.1299 |
| 0.0880 | 1.0032 | 0.852 | 44.71 | 0.1449 |
| 0.1000 | 1.0035 | 0.858 | 45.15 | 0.1590 |
| $T = 308.15$ K | | | | |
| 0.0239 | 0.9981 | 0.737 | 40.82 | 0.1060 |
| 0.0319 | 0.9984 | 0.739 | 41.45 | 0.1093 |
| 0.0558 | 0.9991 | 0.748 | 42.83 | 0.1320 |
| 0.0717 | 0.9996 | 0.753 | 43.45 | 0.1440 |
| 0.0877 | 1.0000 | 0.760 | 44.18 | 0.1610 |
| 0.0997 | 1.0004 | 0.765 | 44.43 | 0.1720 |
| $T = 318.15$ K | | | | |
| 0.0238 | 0.9939 | 0.583 | 38.85 | 0.1789 |
| 0.0317 | 0.9941 | 0.586 | 39.76 | 0.1820 |
| 0.0556 | 0.9949 | 0.594 | 41.39 | 0.2017 |
| 0.0715 | 0.9954 | 0.599 | 42.24 | 0.2094 |
| 0.0873 | 0.9958 | 0.603 | 42.99 | 0.2110 |
| 0.0992 | 0.9962 | 0.605 | 43.40 | 0.2110 |
| 0.015 mol dm ⁻³ of Ag_2SO_4 in aqueous solution | | | | |
| $T = 298.15$ K | | | | |
| 0.0240 | 1.0028 | 0.850 | 46.48 | 0.0599 |
| 0.0320 | 1.0030 | 0.852 | 46.70 | 0.0630 |
| 0.0560 | 1.0036 | 0.865 | 47.26 | 0.1140 |
| 0.0720 | 1.0041 | 0.880 | 47.61 | 0.1666 |
| 0.0879 | 1.0045 | 0.885 | 47.93 | 0.1720 |
| 0.0999 | 1.0048 | 0.898 | 48.05 | 0.2100 |
| $T = 308.15$ K | | | | |
| 0.0239 | 0.9995 | 0.728 | 43.75 | 0.1149 |
| 0.0319 | 0.9998 | 0.734 | 44.73 | 0.1460 |
| 0.0558 | 1.0004 | 0.748 | 45.73 | 0.1960 |
| 0.0718 | 1.0009 | 0.756 | 45.99 | 0.2129 |
| 0.0876 | 1.0013 | 0.764 | 46.34 | 0.2329 |
| 0.0996 | 1.0016 | 0.769 | 46.92 | 0.2380 |
| $T = 318.15$ K | | | | |
| 0.0238 | 0.9948 | 0.599 | 41.23 | 0.2480 |
| 0.0318 | 0.9951 | 0.606 | 41.57 | 0.2800 |
| 0.0555 | 0.9958 | 0.619 | 42.63 | 0.3039 |
| 0.0714 | 0.9962 | 0.629 | 44.24 | 0.3349 |
| 0.0872 | 0.9967 | 0.639 | 44.82 | 0.3600 |
| 0.0991 | 0.9970 | 0.644 | 45.16 | 0.3644 |
| 0.020 mol dm ⁻³ of Ag_2SO_4 in aqueous solution | | | | |
| $T = 298.15$ K | | | | |
| 0.0240 | 1.0041 | 0.825 | 50.87 | 0.0340 |
| 0.0320 | 1.0043 | 0.829 | 51.10 | 0.0540 |
| 0.0560 | 1.0048 | 0.843 | 51.50 | 0.1119 |
| 0.0720 | 1.0052 | 0.850 | 51.76 | 0.1320 |
| 0.0880 | 1.0055 | 0.858 | 51.90 | 0.1539 |
| 0.1000 | 1.0058 | 0.867 | 52.03 | 0.1769 |
| $T = 308.15$ K | | | | |
| 0.0240 | 1.0006 | 0.702 | 49.54 | 0.0790 |
| 0.0319 | 1.0008 | 0.705 | 49.75 | 0.0929 |
| 0.0558 | 1.0014 | 0.715 | 50.39 | 0.1350 |
| 0.0718 | 1.0017 | 0.726 | 50.79 | 0.1770 |
| 0.0877 | 1.0021 | 0.731 | 50.99 | 0.1829 |
| 0.0996 | 1.0024 | 0.739 | 51.12 | 0.2100 |
| $T = 318.15$ K | | | | |
| 0.0239 | 0.9972 | 0.633 | 46.51 | 0.2499 |
| 0.0317 | 0.9974 | 0.638 | 46.83 | 0.2679 |
| 0.0556 | 0.9979 | 0.652 | 48.78 | 0.2999 |
| 0.0715 | 0.9983 | 0.663 | 49.37 | 0.3320 |
| 0.0873 | 0.9987 | 0.673 | 49.89 | 0.3553 |
| 0.0993 | 0.9990 | 0.682 | 50.28 | 0.3769 |

Table 3: Partial molar volumes and the experimental slopes of Eq. 2 for glycine in different aqueous Ag_2SO_4 solutions with corresponding standard deviations at different temperatures.

| T/K | $\varphi_V^0 \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$) | $S_V^* \times 10^6$ ($\text{m}^3 \text{mol}^{-3})^{1/2}$) | σ |
|--|---|--|----------|
| Pure aqueous solution | | | |
| 298.15 | 43.19 ^a | 0.864 ^a | – |
| 308.15 | 43.79 ^b | 0.86 ^b | – |
| 318.15 | 44.17 ^b | 1.77 ^b | – |
| 0.005 mol dm^{-3} of Ag_2SO_4 in aqueous solution | | | |
| 298.15 | 38.32 | 20.12 | 0.004 |
| 308.15 | 34.52 | 30.32 | 0.020 |
| 318.15 | 21.22 | 38.61 | 0.091 |
| 0.010 mol dm^{-3} of Ag_2SO_4 in aqueous solution | | | |
| 298.15 | 40.14 | 15.50 | 0.006 |
| 308.15 | 37.38 | 22.69 | 0.006 |
| 318.15 | 34.65 | 28.15 | 0.007 |
| 0.015 mol dm^{-3} of Ag_2SO_4 in aqueous solution | | | |
| 298.15 | 44.92 | 10.00 | 0.001 |
| 308.15 | 41.34 | 17.55 | 0.001 |
| 318.15 | 36.99 | 26.07 | 0.001 |
| 0.020 mol dm^{-3} of Ag_2SO_4 in aqueous solution | | | |
| 298.15 | 49.80 | 7.13 | 0.001 |
| 308.15 | 47.96 | 10.23 | 0.002 |
| 318.15 | 42.69 | 24.56 | 0.011 |

^a values taken from Ref²¹, ^b values taken from Ref²².

These trends in φ_V^0 values are easy to follow from the trends in φ_V values as listed in Table 2 showing that the φ_V values increase with a rise in both the concentrations of glycine and Ag_2SO_4 in the ternary solutions but decrease as the temperature of these solutions decrease. Interestingly φ_V^0 values decreased on the introduction of Ag_2SO_4 in the aqueous solutions (from 0 to 0.005 mol dm^{-3} of Ag_2SO_4 solutions), but after that φ_V^0 values increased monotonically with further addition of Ag_2SO_4 in the aqueous solutions. This is probably due to the perturbation of the arrangement of water molecules in bulk water by the electric field of the constituent ions.

The parameter S_V^* is the volumetric virial coefficient characterizing the pairwise interaction of solvated species in solution,^{23, 24} the sign of S_V^* is determined by the interaction between the solute species. In the present study, S_V^* is found to be positive for all the glycine solutions. For zwitter-ionic amino acids the positive value of S_V^* suggest that the pairwise interaction is dominated by the interaction of the charged functional groups. A perusal of Table 3 shows that S_V^* values are positive and increase as the temperature increases but decrease as the amount of Ag_2SO_4 in the aqueous solutions increases.

The temperature dependence of partial molar volumes (φ_V^0) was expressed by the following relation,

$$\varphi_V^0 = a_0 + a_1T + a_2T^2 \quad (3)$$

The values of the coefficients a_0 , a_1 , a_2 of the above equation for different glycine solutions are listed in Table 4.

Table 4: Values of various coefficients of Eq. 3 for glycine in different aqueous Ag_2SO_4 solutions.

| Molarity of Ag_2SO_4 in aqueous solution (mol dm^{-3}) | $a_0 \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$) | $a_1 \times 10^6$ ($\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$) | $a_2 \times 10^6$ ($\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$) |
|--|---|---|---|
| 0 | –75.761 ^a | 0.727 ^a | –0.001 ^a |
| 0.005 | –4214.200 | 28.431 | –0.047 |
| 0.010 | 137.040 | –0.373 | 0.001 |
| 0.015 | –198.360 | 1.952 | –0.004 |
| 0.020 | –1468.100 | 10.195 | –0.017 |

^a values calculated using φ_V^0 values from Ref²¹ and Ref²².

The partial molar expansibilities φ_E^0 can be obtained by the following equation,²⁵

$$\varphi_E^0 = \left(\delta\varphi_V^0 / \delta T \right)_P = a_1 + 2a_2T \quad (4)$$

The φ_E^0 values given in Table 5, for different ternary solutions at different temperatures, show that φ_E^0 values decrease as the temperature and concentrations of Ag_2SO_4 in the aqueous solutions increases.

According to Hepler,²⁶ the sign of $(\delta\varphi_E^0/\delta T)_P$ is a better criterion in characterizing the long-range structure making or breaking ability of the solutes in solution. The general thermodynamic expression is as follows:

$$\left(\delta\varphi_E^0 / \delta T \right)_P = \left(\delta^2 \varphi_V^0 / \delta T^2 \right)_P = 2a_2 \quad (5)$$

If the sign of $(\delta\varphi_E^0/\delta T)_P$ is positive or small negative, the solute is a structure-maker; otherwise it is a structure breaker. It is seen from Table 5, glycine predominantly acts as a structure maker and its structure-making ability generally increases with an increase in both the temperature and the amount of Ag_2SO_4 in the aqueous solutions increases.

3. 2. Hydration Number

The number of water molecules (N_w) hydrated to glycine at 298.15 K, can be estimated from the electrostriction partial molar volume $\varphi_V^0(\text{elect})$ ²² using the relation:

$$N_w = \frac{\varphi_V^0(\text{elect})}{(\varphi_e^0 - \varphi_b^0)} \quad (6)$$

where φ_e^0 is the molar volume of the electrostricted water and φ_b^0 is the molar volume of bulk water. The value of $(\varphi_e^0 - \varphi_b^0)$ is calculated²² to be $-3.3 \text{ cm}^3 \text{ mol}^{-1}$ at 298.15 K. The

Table 5: Limiting partial molar expansibilities for glycine in different aqueous Ag₂SO₄ solutions at different temperatures.

| Molarity of Ag ₂ SO ₄ in aqueous solution (mol dm ⁻³) | $\phi_E^0 \times 10^6$ (m ³ mol ⁻¹ K ⁻¹) | | | $\left(\frac{\partial \phi_E^0}{\partial T}\right)_p \times 10^6$ (m ³ mol ⁻¹ K ⁻¹) |
|---|--|--------------------|--------------------|---|
| | 298,15 K | 308,15 K | 318,15 K | |
| 0 | 0.071 ^a | 0.049 ^a | 0.027 ^a | -0.002 |
| 0.005 | 0.405 | -0.535 | -1.475 | -0.094 |
| 0.010 | 0.223 | 0.243 | 0.263 | 0.002 |
| 0.015 | -0.433 | -0.513 | -0.593 | -0.008 |
| 0.020 | -0.058 | -0.282 | -0.622 | -0.034 |

^a values calculated using ϕ_V^0 values from Ref²¹ and Ref²².

$\phi_V^0(\text{elect})$ values can be calculated²² from the intrinsic partial molar volumes of the amino acids, ϕ_V^0 ^{27,28} and experimentally determined ϕ_V^0 values, as follows:

$$\phi_V^0(\text{Glycine}) = \phi_V^0(\text{int}) + \phi_V^0(\text{elect}) \quad (7)$$

The obtained N_w values for glycine at 298.15 K are 2.7, 4.1, 3.5 and 2.1 in pure aqueous solution, 0.005 mol dm⁻³ aqueous Ag₂SO₄ solution, 0.010 mol dm⁻³ aqueous Ag₂SO₄ solution, 0.015 mol dm⁻³ aqueous Ag₂SO₄ solution and 0.020 mol dm⁻³ aqueous Ag₂SO₄ solution, respectively. This means that N_w varies with the solvent composition showing a tendency to decrease with an increase in the concentration of Ag₂SO₄ in the aqueous solutions increases; although there was an initial increase of N_w for 0.005 mol dm⁻³ aqueous Ag₂SO₄ solutions on shifting from pure aqueous solutions. This increase in N_w indicates that the increase in the interaction of hydrophobic group of glycine with those of the salt does not reduce the electrostriction of water molecules initially, but leads to an increase in the hydration number N_w but thereafter N_w gradually decreases as the molarity of Ag₂SO₄ in the ternary solutions increase indicating enhanced electrostriction of water molecules due to greater ionic concentrations.

3. 3. Standard Transfer Volume

Standard transfer volume $\Delta\phi_V^0$ of glycine from pure water to aqueous of Ag₂SO₄ solutions is defined by:

$$\Delta\phi_V^0 = \phi_V^0(\text{Glycine} + \text{Ag}_2\text{SO}_4 + \text{Water}) - \phi_V^0(\text{Water}) \quad (8)$$

The value of $\Delta\phi_V^0$, by definition, is free from solute-solute interactions and therefore provides information regarding solute-cosolute interaction.⁸ Table 6 shows that $\Delta\phi_V^0$ values are generally negative and increases monotonically with the concentration of Ag₂SO₄ in the solutions under investigation. In general, the interactions between glycine and Ag₂SO₄ can be summarized as: (i) ion-ion interaction between Ag⁺ and COO⁻ group, (ii) ion-ion inter-

action between SO₄²⁻ and NH₃⁺ groups; (iii) ion-nonpolar group interactions.

Table 6: Partial molar volumes of transfer from water to different aqueous Ag₂SO₄ solutions for glycine at different temperatures.

| Molarity of Ag ₂ SO ₄ in aqueous solution (mol dm ⁻³) | $\phi_V^0 \times 10^6$ (m ³ mol ⁻¹) | $\Delta\phi_V^0 \times 10^6$ (m ³ mol ⁻¹) |
|---|--|--|
| T = 298.15 K | | |
| 0 | 43.19 ^a | 0 |
| 0.005 | 38.325 | -4.865 |
| 0.010 | 40.136 | -3.054 |
| 0.015 | 44.918 | 1.728 |
| 0.020 | 49.802 | 6.612 |
| T = 308.15 K | | |
| 0 | 43.79 ^b | 0 |
| 0.005 | 34.524 | -9.266 |
| 0.010 | 37.379 | -6.411 |
| 0.015 | 41.337 | -2.453 |
| 0.020 | 47.958 | 4.168 |
| T = 318.15 K | | |
| 0 | 44.17 ^b | 0 |
| 0.005 | 21.219 | -22.951 |
| 0.010 | 34.654 | -9.516 |
| 0.015 | 36.994 | -7.176 |
| 0.020 | 42.690 | -1.48 |

^a values taken from Ref²¹ ^b values taken from Ref²².

According to the cosphere overlap model of Gurney²⁹ whereas interactions of type (i) and (ii) lead to positive $\Delta\phi_V^0$ values, type (iii) would lead to negative $\Delta\phi_V^0$ values. Thus, the negative $\Delta\phi_V^0$ values for glycine indicate that ion-hydrophobic and hydrophobic-hydrophobic interactions predominate over the ion-hydrophilic and hydrophilic-hydrophilic interactions. The $\Delta\phi_V^0$ values for glycine at different temperatures have been depicted in Figure 1 as a function of the molarity Ag₂SO₄ in the ternary solutions.

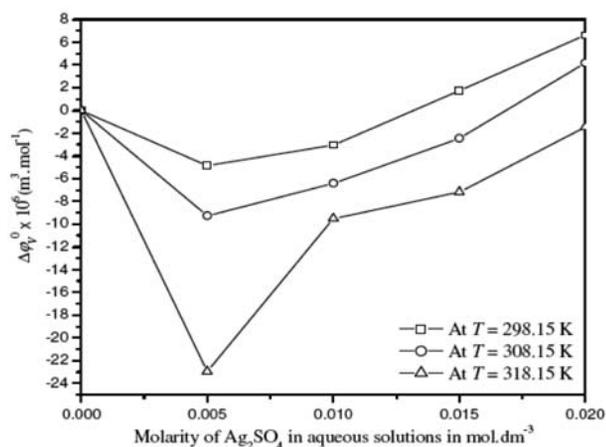


Figure 1: Plots of partial molar volumes of transfer ($\Delta\phi_V^0$) from water to different aqueous Ag_2SO_4 solutions for glycine at different temperatures.

However, since SO_4^{2-} ion remains comparatively more hydrated than Ag^+ ion in aqueous solutions, they can affect the partial molar volume of glycine to varying degrees. Anyway, the observed trend can also be explained with the following equation:^{3, 12}

$$\phi_V^0 = \phi_{VW} + \phi_{Void} - \phi_S \quad (9)$$

where ϕ_{VW} is the van der Waals volume, ϕ_{Void} is the volume associated with voids or empty space, and ϕ_S the shrinkage volume due to electrostriction. Assuming the ϕ_{VW} and ϕ_{Void} have the same magnitudes in water and in aqueous Ag_2SO_4 solutions for class of solutes,³⁰ the observed negative $\Delta\phi_V^0$ values for glycine indicate an increase in shrinkage volume in presence of Ag_2SO_4 and this trend increased with increased temperatures.

3. 4. Viscosity B-coefficient

The viscosity data of the experimental solutions of glycine have been analyzed using the Jones-Dole equation,³¹

$$(\eta/\eta_0 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad (10)$$

where $\eta = \eta/\eta_0$, and η are the viscosities of the solvent and solution, respectively, and c is the molar concentration of a solution. A and B are the Jones-Dole constants estimated by a least-squares method and reported in Table 7.

The viscosity B -coefficient²¹ reflects the effects of solute–solvent interactions on the solution viscosity and it is indeed a valuable tool to provide information concerning the solvation of solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules. Table 7 shows that the values of the viscosity B -co-

Table 7: Values of Viscosity A and B coefficients for glycine in different aqueous Ag_2SO_4 solutions at different temperatures.

| Viscosity coefficients | T = 298.15 K | T = 308.15 K | T = 318.15 K |
|--|---------------------|---------------------|--------------------|
| Pure aqueous solution | | | |
| A ($10^6 \text{ m}^{3/2} \text{ mol}^{-1/2}$) | – | – | – |
| B ($10^6 \text{ m}^3 \text{ mol}^{-1}$) | 0.134 ^a | 0.142 ^a | 0.151 ^a |
| 0.005 mol dm ⁻³ of Ag_2SO_4 in aqueous solution | | | |
| A ($10^6 \text{ m}^{3/2} \text{ mol}^{-1/2}$) | 0.008 (± 0.001) | 0.078 (± 0.002) | 0.113 (± 0.001) |
| B ($10^6 \text{ m}^3 \text{ mol}^{-1}$) | 0.289 (± 0.001) | 0.248 (± 0.002) | 0.109 (± 0.001) |
| 0.010 mol dm ⁻³ of Ag_2SO_4 in aqueous solution | | | |
| A ($10^6 \text{ m}^{3/2} \text{ mol}^{-1/2}$) | -0.001 (± 0.002) | 0.038 (± 0.001) | 0.145 (± 0.000) |
| B ($10^6 \text{ m}^3 \text{ mol}^{-1}$) | 0.494 (± 0.003) | 0.412 (± 0.001) | 0.223 (± 0.001) |
| 0.015 mol dm ⁻³ of Ag_2SO_4 in aqueous solution | | | |
| A ($10^6 \text{ m}^{3/2} \text{ mol}^{-1/2}$) | -0.098 (± 0.003) | 0.006 (± 0.001) | 0.143 (± 0.004) |
| B ($10^6 \text{ m}^3 \text{ mol}^{-1}$) | 0.945 (± 0.001) | 0.762 (± 0.003) | 0.714 (± 0.001) |
| 0.020 mol dm ⁻³ of Ag_2SO_4 in aqueous solution | | | |
| A ($10^6 \text{ m}^{3/2} \text{ mol}^{-1/2}$) | -0.100 (± 0.001) | -0.050 (± 0.002) | 0.128 (± 0.001) |
| B ($10^6 \text{ m}^3 \text{ mol}^{-1}$) | 0.870 (± 0.001) | 0.812 (± 0.003) | 0.771 (± 0.001) |

^a values taken from Ref³² and standard errors are given in parentheses.

efficient for glycine in the studied solvent systems are positive, thereby suggesting the presence of strong solute–solvent interactions which increase as the molarity of Ag_2SO_4 in the solutions increase but decrease as the temperature of the solutions increase. The values of the A -coefficient are indicative of solute–solute interactions and in the present study they are in line with the viscosity B -coefficients for glycine in different aqueous Ag_2SO_4 solutions at the experimental temperatures. Viscosity B -coefficients of transfer (ΔB) from water to different aqueous Ag_2SO_4 solutions have been determined using the relation:

$$\Delta B = B(\text{Aqueous } \text{Ag}_2\text{SO}_4 \text{ solution}) - B(\text{Water}) \quad (11)$$

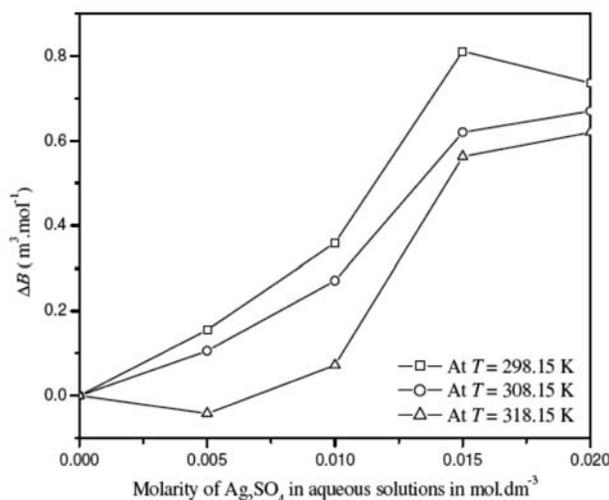
The ΔB values shown in Table 8 as well as depicted in Figure 2 as a function of the molarity Ag_2SO_4 in the ternary solutions at different temperatures are in line with the results obtained from $\Delta\phi_V^0$ values discussed above.

The viscosity data have also been analyzed on the basis of transition state theory for the relative viscosity of the solutions as suggested by Feakins et al.³³ using the relation,

$$\Delta\mu_2^{0\ddagger} = \Delta\mu_1^{0\ddagger} + RT(1000B + \phi_2^0 - \phi_1^0)/\phi_1^0 \quad (12)$$

Table 8: Viscosity B -coefficients of transfer from water to different aqueous Ag_2SO_4 solutions for glycine at different temperatures.

| Molarity of Ag_2SO_4 in aqueous solution (mol dm^{-3}) | B ($\text{m}^3 \text{mol}^{-1}$) | ΔB ($\text{m}^3 \text{mol}^{-1}$) |
|---|--------------------------------------|---|
| $T = 298.15 \text{ K}$ | | |
| 0 | 0.134 ^a | 0 |
| 0.005 | 0.289 | 0.155 |
| 0.010 | 0.494 | 0.360 |
| 0.015 | 0.945 | 0.811 |
| 0.020 | 0.870 | 0.736 |
| $T = 308.15 \text{ K}$ | | |
| 0 | 0.142 ^a | 0 |
| 0.005 | 0.248 | 0.106 |
| 0.010 | 0.413 | 0.271 |
| 0.015 | 0.762 | 0.620 |
| 0.020 | 0.812 | 0.670 |
| $T = 318.15 \text{ K}$ | | |
| 0 | 0.151 ^a | 0 |
| 0.005 | 0.109 | -0.042 |
| 0.010 | 0.223 | 0.072 |
| 0.015 | 0.714 | 0.563 |
| 0.020 | 0.771 | 0.620 |

^a values taken from Ref³².**Figure 2:** Plots of viscosity B -coefficients of transfer (ΔB) from water to different aqueous Ag_2SO_4 solutions for glycine at different temperatures.

here φ_1^0 and φ_2^0 are the partial molar volumes of the solvent and solute, respectively. The contribution per mole of the solute to the free energy of activation of viscous flow, $\Delta\mu_2^{0\neq}$ of the solutions was determined from the above relation. The free energy of activation of viscous flow for the solvent mixture, $\Delta\mu_1^{0\neq}$, is given by the relation:^{33, 34}

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln(\eta_0 \varphi_1^0 / h N_A) \quad (13)$$

where N_A is the Avogadro's number and the other symbols have their usual significance. The values of the parameters $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ are reported in Table 9 which shows that $\Delta\mu_1^{0\neq}$ is almost constant at all temperatures and solvent compositions.

It means that $\Delta\mu_2^{0\neq}$ is dependent mainly on the values of viscosity B -coefficients and $(\varphi_{V,2}^0 - \varphi_{V,1}^0)$ terms. But $\Delta\mu_2^{0\neq}$ values were found to be positive at all the experimental temperatures and this suggests that the process of viscous flow becomes difficult as the temperature and molarity of Ag_2SO_4 in solutions increases. Hence the formation of the transition state becomes less favourable.³³ According to Feakins et al.,³³ $\Delta\mu_2^{0\neq} > \Delta\mu_1^{0\neq}$ for solutes having positive viscosity B -coefficients indicates stronger solute-solvent interactions, suggesting the formation of a transition state which is accompanied by the rupture and distortion of the intermolecular forces in the solvent struc-

Table 9: Values of $\varphi_{V,2}^0 - \varphi_{V,1}^0$, $\Delta\mu_1^{0\neq}$, $\Delta\mu_2^{0\neq}$, $T\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ for glycine in different aqueous.

| Parameters | 298.15 K | 308.15 K | 318.15 K |
|---|----------|----------|----------|
| Pure aqueous solution^a | | | |
| $(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$) | 25.03 | 25.58 | 25.79 |
| $\Delta\mu_1^{0\neq}$ (kJ mol^{-1}) | 9.175 | 8.944 | 8.761 |
| $\Delta\mu_2^{0\neq}$ (kJ mol^{-1}) | 30.891 | 32.524 | 34.205 |
| $T\Delta S_2^{0\neq}$ (kJ mol^{-1}) | -49.403 | -51.06 | -52.717 |
| $\Delta H_2^{0\neq}$ (kJ mol^{-1}) | -18.512 | -18.536 | -18.512 |
| 0.005 mol dm⁻³ of Ag_2SO_4 in aqueous solution | | | |
| $(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$) | 20.21 | 16.35 | 2.86 |
| $\Delta\mu_1^{0\neq}$ (kJ mol^{-1}) | 8.749 | 8.536 | 8.304 |
| $\Delta\mu_2^{0\neq}$ (kJ mol^{-1}) | 51.026 | 45.747 | 24.396 |
| $T\Delta S_2^{0\neq}$ (kJ mol^{-1}) | 396.987 | 410.302 | 423.617 |
| $\Delta H_2^{0\neq}$ (kJ mol^{-1}) | 448.013 | 456.049 | 448.013 |
| 0.010 mol dm⁻³ of Ag_2SO_4 in aqueous solution | | | |
| $(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$) | 22.05 | 19.23 | 16.33 |
| $\Delta\mu_1^{0\neq}$ (kJ mol^{-1}) | 8.952 | 8.957 | 8.624 |
| $\Delta\mu_2^{0\neq}$ (kJ mol^{-1}) | 79.675 | 69.943 | 43.235 |
| $T\Delta S_2^{0\neq}$ (kJ mol^{-1}) | 543.229 | 561.449 | 579.669 |
| $\Delta H_2^{0\neq}$ (kJ mol^{-1}) | 622.904 | 631.392 | 622.904 |
| 0.015 mol dm⁻³ of Ag_2SO_4 in aqueous solution | | | |
| $(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$) | 26.85 | 23.22 | 18.69 |
| $\Delta\mu_1^{0\neq}$ (kJ mol^{-1}) | 9.025 | 8.916 | 8.668 |
| $\Delta\mu_2^{0\neq}$ (kJ mol^{-1}) | 142.36 | 119.87 | 114.471 |
| $T\Delta S_2^{0\neq}$ (kJ mol^{-1}) | 415.77 | 429.715 | 443.66 |
| $\Delta H_2^{0\neq}$ (kJ mol^{-1}) | 558.13 | 549.585 | 558.13 |
| 0.020 mol dm⁻³ of Ag_2SO_4 in aqueous solution | | | |
| $(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$) | 31.77 | 29.86 | 24.43 |
| $\Delta\mu_1^{0\neq}$ (kJ mol^{-1}) | 8.958 | 8.834 | 8.803 |
| $\Delta\mu_2^{0\neq}$ (kJ mol^{-1}) | 132.917 | 128.023 | 124.061 |
| $T\Delta S_2^{0\neq}$ (kJ mol^{-1}) | 132.021 | 136.449 | 140.877 |
| $\Delta H_2^{0\neq}$ (kJ mol^{-1}) | 264.938 | 264.472 | 264.938 |

^a values calculated using B -values from Ref³².

ture.³³ The larger is the value of $\Delta\mu_2^{0\neq}$, the greater is the structure-making tendency of the solute, and the positive values of $\Delta\mu_2^{0\neq}$ for glycine in the different aqueous Ag_2SO_4 solutions suggests glycine to be a net structure promoter in these ternary mixtures.

The entropy of activation for electrolytic solutions has been calculated relation:³³

$$\Delta S_2^{0\neq} = -d(\Delta\mu_2^{0\neq})/dT \quad (14)$$

where $\Delta S_2^{0\neq}$ has been obtained from the negative slope of the plots of $\Delta\mu_2^{0\neq}$ against T by using a least squares treatment. The activation enthalpy ($\Delta H_2^{0\neq}$) has been calculated using the relation:³³

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \quad (15)$$

The value of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ are listed in Table 9 and they were found to be positive for all the experimental solutions at all the temperatures suggesting that the transition state is associated with bond breaking and decrease in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state.^{33, 34}

4. Conclusion

In summary, φ_V^0 and viscosity B -coefficient values for glycine indicate the presence of strong solute-solvent interactions, which further strengthened at higher molarities of Ag_2SO_4 in the ternary solutions but decrease at higher temperatures. Also the trend in $(\delta\varphi_E^0/\delta T)_P$, N_W and $\Delta\mu_2^{0\neq}$ values for glycine in the different aqueous Ag_2SO_4 solutions suggest glycine to be a net structure promoter in these ternary mixtures.

5. References

- G. R. Hedwig, and H. Hoiland, *J. Chem. Thermody.* **1993**, 25, 349–354.
- G. R. Hedwig, *J. Chem. Soc. Faraday Trans.* **1993**, 2761–2768.
- R. Bhat, and J. C. Ahluwalia, *J. Phys. Chem.* **1985**, 89, 1099–1105.
- T. V. Chalikan, A. P. Sarvazyan, and K. J. Breslauer, *J. Phys. Chem.* **1993**, 97, 13017–13026.
- P. H. Von Hippel, and T. Schleich, *Acc. Chem. Res.* **1969**, 2, 257–265.
- W. P. Jencks, *Catalysis in Chemistry and Enzymology*, McGraw Hill, New York 1969, p. 351.
- K. Beliali, and E. Agranci, *J. Solution. Chem.* **1990**, 19, 867–882.
- Z. Yan, J. Wan, H. Hang, and D. Liu, *J. Solution. Chem.* **1998**, 27, 473–483.
- R. K. Wadi, and R. K. Goyal, *J. Solution. Chem.* **1992**, 21, 163–170.
- X. Wang, L. Xu, R. S. Lin, and D. Z. Sun, *Acta. Chem. Sin.* **2004**, 62, 1405–1408.
- T. Banerjee, and N. Kishor, *J. Solution. Chem.* **2005**, 35, 137–153.
- B. Sinha, V. K. Dakua, and M. N. Roy, *J. Chem. Eng. Data* **2007**, 52, 1768–1772.
- T. E. Creighton, *Curr. Opin. Struct. Biol.* **1991**, 1, 5–16.
- T. Arakwa, and S. N. Timasheff, *Biochemistry.* **1984**, 23, 5912–5923.
- Jr. Raymond F. Greene, and C. Nick Pace, *J. Biol. Chem.* **1974**, 249, 5388–5393.
- G. Velicelebi, and J. M. Sturtevant, *Biochemistry.* **1979**, 18, 1180–1186.
- M. N. Roy, and D. K. Hazra, *J. Chem. Technol.* **1994**, 1, 93–97.
- M. N. Roy, B. Sinha, and V. K. Dakua, *J. Chem. Eng. Data* **2006**, 51, 590–594.
- M. N. Roy, and B. Sinha, *J. Mol. Liq.* **2007**, 133, 89–99.
- D. O. Masson, *Philos. Mag.* **1929**, 8, 218–223.
- F. J. Millero, A. L. Surdo, and C. Shin, *J. Phys. Chem.* **1978**, 82, 784–792.
- T. S. Banipal, and P. Kapoor, *J. Indian. Chem. Soc.* **1999**, 7, 431–437.
- J. E. Desnoyers, *Pure. Appl. Chem.* **1982**, 54, 1469–1478.
- T. E. Leslie, and T. H. Lilley, *Biopolymers*, **1985**, 24, 695–710.
- B. Sinha, B. K. Sarkar, and M. N. Roy, *J. Chem. Thermody.* **2008**, 40, 394–400.
- G. Hepler, *Can. J. Chem.* **1969**, 47, 4617–4622.
- E. Berlin, M. J. Pallansch, *J. Phys. Chem.* **1968**, 72, 1887–1889.
- F. T. Gucker, W. L. Ford, and C. E. Moser, *J. Phys. Chem.* **1939**, 43, 153–168.
- R. W. Gurney, *Ionic Processes in Solution*, McGraw-Hill, New York **1953**.
- A. K. Mishra, and J. C. Ahluwalia, *J. Chem. Soc. Faraday Trans. 1* **1981**, 77, 1469–1483.
- G. Jones, and M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950–2964.
- T. S. Banipal, A. Bhatia, P. K. Banipal, G. Singh, and D. Kaur, *J. Indian. Chem. Soc.* **2004**, 81, 126–131.
- D. Feakins, D. J. Freemantle, K. G. Lawrence, *J. Chem. Soc., Faraday Trans. 1* **1974**, 70, 795–806.
- S. Glasstone, K. Laidler, and H. Eyring, *The Theory of Rate processes*, McGraw-Hill, New York **1941**.

Povzetek

Pri 298.15, 308.15 in 318.15 K smo izmerili gostote in viskoznosti raztopin glicina v 0.005, 0.010, 0.015 in 0.020 molarne vodnih raztopinah srebrovega sulfata (Ag_2SO_4) v širokem koncentracijskem območju. Iz eksperimentalnih podatkov smo izračunali navidezne molske volumne (φ_V) in koeficiente viskoznosti B za glicin v preiskovanih raztopinah. Koncentracijsko odvisnost φ_V smo opisali z Massonovo enačbo ter določili navidezne molske volumne pri neskončnem razredčenju φ_V^* ter naklon S_V^* . Iz vrednosti dobljenih parametrov smo sklepali na interakcije topilo-topljenec ter topljenec-topljenec v raztopinah. Podatke za viskoznost smo analizirali z uporabo Jones-Dolejeve enačbe; dobljena parametra A in B pa nam spet dajeta informacije o interakcijah v raztopinah. Določili smo tudi standardne volumne prenosa ($\Delta\varphi_V$) ter B-koeficiente prenosa (ΔB) za prenos glicina iz vode v vodno raztopino Ag_2SO_4 ter tudi z njihovo pomočjo proučevali različne interakcije v ternarnih raztopinah. Predznak izraza $(\delta^2\varphi_V^0/\delta T^2)_p$ je merilo za »structure making« oz. »structure braking« efekt glicina. Izračunali smo tudi aktivacijske parametre viskoznostnega toka za ternarne raztopine ter jih razložili z teorijo prehodnih stanj