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MOLECULAR INTERACTION STUDIES IN TERNARY GLYCINE + (AQUEOUS THIOUREA) SOLUTIONS AT 298.15 K

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ABSTRACT

Partial molar volumes (φ^0_v) and viscosity *B*-coefficients of glycine + aqueous thiourea solutions (0.5 and 1.5 mol·dm^{-3}) were determined at 298.15 K using Masson ($\varphi_v = \varphi^0_v + S_v \times \sqrt{c}$) and Jones-Dole relation ($\eta_r\text{-}1/\sqrt{c} = A + B \times \sqrt{c}$), respectively. Partial molar volumes of transfer ($\Delta_{tr}\varphi^0_v$) and *B*-coefficients of transfer of glycine at infinite dilution from pure water to aqueous-thiourea solutions were calculated. Strong solute-solvent interactions strengthening with thiourea concentration and hydrophilic-hydrophilic as well as ion-hydrophilic or ion-polar interactions were observed in the these systems.

Key words: Glycine, Thiourea, Partial molar volumes, Viscosity B-coefficients.

INTRODUCTION

Amino acids are building blocks of protein and they contain both amino (NH_2) and acid (COOH) groups. Glycine is a smallest amino acid found in proteins and it is precursor to proteins as well as it is a building block to number of natural products and has pharmaceutical, industrial and research applications. Glycine can fit into both; hydrophilic and hydrophobic environments. It can form H-bond with water through -NH_2 and –COOH groups. Physico-chemical investigation of dissolution and solvation of amino acid like glycine in aqueous solution of thiourea are of great significance. Numbers of workers have studied the aqueous glycine system and hydration structure of glycine in different environments[1-5]. Densities, partial molar volumes and heat capacities of glycine in aqueous magnesium chloride solutions at different temperatures have been studied by Lark et al.[6], transfer volumes of glycine, from water to 1,2-butanediol-water mixtures at 298.15 K were

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studied by Xu et al.[7] and influence of hydrotropic agents on the solute-solvent interactions in aqueous solutions of glycine at different temperatures were studied by Pattnaik et al.[8] Physico-chemical properties of amino acids in aqueous, aqueous electrolytes and organic solutes have been extensively investigated[9-11]. Volumetric methods are widely used to understand the solute-solvent interactions because of their high sensitivity[12,13]. Intermolecular interactions have been largely investigated through thermodynamic methods like density, viscosity and the refractive index of solutions[14,15].

In continuation with our program to understand the structure and molecular interactions in solution[16-21], we report the systematic study of volumetric and viscometric behavior of glycine with different concentrations in 0.5 and 1.5 $mol \cdot dm^{-3}$ aqueous thiourea solutions at 298.15 K.

EXPERIMENTAL

Glycine (sd fine, AR grade, > 99.0%) was used. Aqueous stock solutions of 0.5 and 1.5 $mol \cdot dm^{-3}$ thiourea were prepared in calibrated volumetric flasks by dissolving accurate quantity of thiourea in double distilled water. Glycine solutions with different concentrations were prepared in aqueous thiourea stock solutions by dissolving accurate amounts of glycine. The solutions were always kept in airtight flasks. Density measurements were carried out using single capillary pycnometer and weighing was done on single pan, electronic balance (± 0.001 g) using a weighing scoop. Pycnometer was calibrated with benzene and distilled water at 298.15 K. Pycnometer was kept in transparent walled constant temperature water bath for 15 min to attain thermal equilibrium. In order to get the accurate results, three sets of density measurements were performed. Viscosity measurements were carried out using Ostwald viscometer by flow time method at 298.15 K and atmospheric pressure. Viscometer was kept in the transparent walled constant temperature water bath at experimental temperature for 15 min to attain the thermal equilibrium. Flow time was recorded using electronic digital stop watch (± 0.01s) and average of three flow times was considered for calculation of viscosity.

RESULTS AND DISCUSSION

Variation in density (ρ) and viscosity (η) with concentration of glycine for glycine + aqueous thiourea solutions at 298.15 K are graphically presented in Fig. 1 and 2. It is seen that, density and viscosity increased with increase in concentration of glycine in aqueous 0.5

and 1.5 mol·dm^{-3} thiourea, which is due to change in volume, modification in the structure and existence of molecular interactions in solutions. Apparent molar volume (φ_v) of glycine was calculated from density data[22-25]. Calculated φ_v values with glycine concentration are presented in Fig. 3. The φ_v values are positive and increased with concentration of both; glycine in 0.5 and 1.5 mol·dm^{-3} aqueous thiourea solutions, which indicate strong solute-solvent interactions strengthening with glycine concentration. The φ_v of glycine in water (43.16 cm^3 mol^{-1}) is less than its φ_v in aqueous thiourea solutions. Hydrophilic-ionic or hydrophilic-hydrophilic interactions in glycine + aqueous thiourea solutions results in reduction of electrostriction effect and enhancement of overall water structure[26].

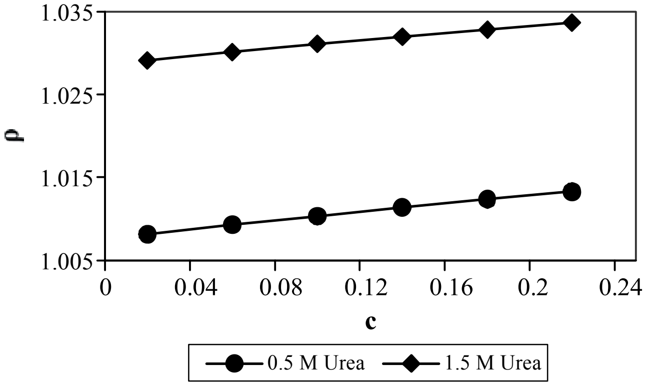

Fig. 1: Variation in density (ρ) with concentration of glycine in ternary glycine + {aqueous-thiourea} solutions at 298.15 K

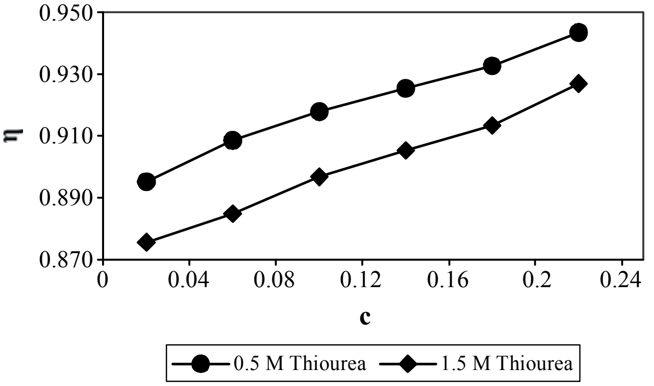

Fig. 2: Variation in viscosity (η) with concentration of glycine in ternary glycine + {aqueous-thiourea} solutions at 298.15 K

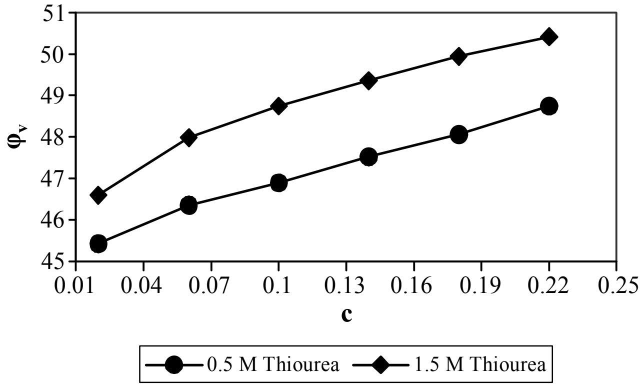

Fig. 3: Variation in apparent molar volume (φ_v) with concentration of in ternary glycine + {aqueous-thiourea} solutions at 298.15 K

Concentration dependence of φ_v was fitted to Massons linear relation[27,28] and from the plots of φ_v and $\sqrt{c}$ (Fig. 4), S_v and φ^0_v was determined as slope and intercept, respectively and reported in Table 1. The φ^0_v is partial molar volume at infinite dilution and it represents solute-solvent interactions and S_v represents solute-solute interactions. The φ^0_v of aqueous-glycine solution at 298.15 K was found to be 43.16 $cm^3 \cdot mol^{-1}$, which is in good agreement with earlier work[29]. The φ^0_v of glycine increased with addition of thiourea in solution compared to in water and further increased with thiourea concentration, which is due to perturbation in the arrangement of water molecules in bulk water by polar effects of thiourea.

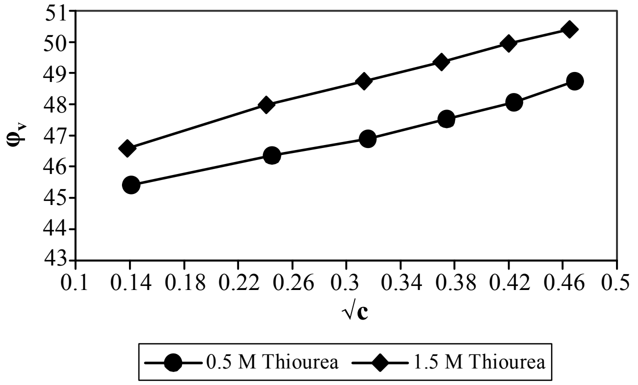

Fig. 4: Graphical determination of φ^0_v and S_v for glycine + {aqueous-thiourea} solutions from φ_v vs. $\sqrt{c}$ plot using Masson's relation at 298.15 K

The φ^0_v values for all studied systems are positive, which indicates the presence of strong solute-solvent interactions in solution and these interactions strengthens upon addition of thiourea[30]. Solute-solute interactions are present but these interactions are weak, which can be recognized from small positive values of S_v compared to φ^0_v. Glycine has zwiterionic structure and therefore, positive values of S_v suggests that pairwise interactions dominates over charged functional groups.

Table 1: The φ^0_v, S_v and $\Delta_{tr}\varphi^0_v$ for glycine + {aqueous-thiourea} solutions at 298.15 K

Property/System	Glycine + {Aqueous 0.5 $mol \cdot dm^{-3}$ thiourea}	Glycine + Aqueous 1.5 $mol \cdot dm^{-3}$ thiourea}
φ^0_v ($cm^3 \cdot mol^{-1}$)	43.92	45.08
S_v ($cm^3 \cdot Kg^{3/2} \cdot mol^{-3/2}$)	9.88	11.59
$\Delta_{tr}\varphi^0_v$ ($cm^3 \cdot mol^{-1}$)	0.76	1.92

Partial molar volumes of transfer ($\Delta_{tr}\varphi^0_v$) at infinite dilution from pure water (43.16 cm^3 mol^{-1}) to aqueous thiourea were calculated[30]. The $\Delta_{tr}\varphi^0_v$ is due to resultant electrostriction because of solute-solvent interaction[31]. Values $\Delta_{tr}\varphi^0_v$ are reported in Table 1. The $\Delta_{tr}\varphi^0_v$ values are positive, which is attributed to decrease in volume of shrinkage because of interactions between glycine and thiourea and existence of hydrophilic-hydrophilic interaction as per cosphere overlap model developed by Gurney[32] and ion-hydrophilic or ion-polar interactions.

This is also supported from positive value of slope (S_v) of Massons plots. Reduction in electrostriction occurs due to less hydration of glycine in presence of thiourea as thiourea takes water molecule to hydrate and glycine will leave with less water molecules, which enhances structure of water. Hydration of glycine decreases due to existence of solute-co-solute ionic/polar-hydrophilic interactions.

The result also indicates absence of hydrophilic-hydrophobic interactions. Positive $\Delta_{tr}\varphi^0_v$ values indicate dominating hydrophilic-hydrophilic or ion-hydrophilic interactions during the overlap of hydration cospheres and strengthening of these interactions with thiourea concentration.

Relative viscosity ($\eta_r = \eta/\eta_0$) was calculated and fitted to Jones-Dole relation and viscosity-A and B coefficients were determined as intercept and slope of the plot η_r-$1/\sqrt{c}$ versus $\sqrt{c}$ (Fig. 5). Graphical A and B viscosity coefficients are reported in Table 2.

Strong solute-solvent interactions are confirmed from the positive values of B-coefficient. The values of viscosity A-coefficient indicates weak solute-solute interactions compared to solute-solvent interactions.

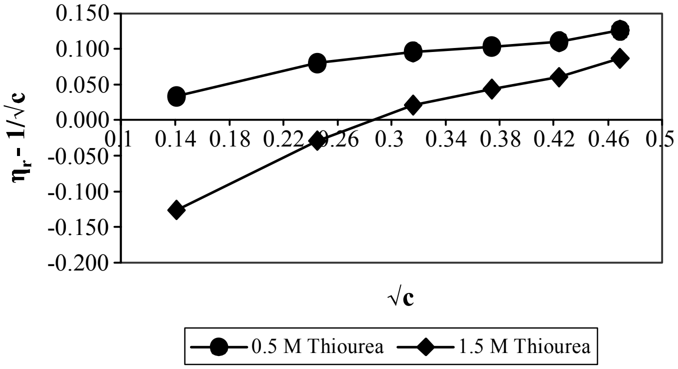

Fig. 5: Jones-Dole plots (η_r-1/√*c* versus √*c*) for ternary glycine + {aqueous-thiourea} solutions at 298.15 K

Table 2: Viscosity *A* and *B*-coefficients for ternary glycine + {aqueous-thiourea} solutions at 298.15 K

Property/System	Glycine + {Aqueous 0.5 mol·dm^{-3} thiourea}	Glycine + {Aqueous 1.5 mol·dm^{-3} thiourea}
A (dm$^{3/2}$ mol$^{-1/2}$)	0.006	-0.196
B (dm^3 mol^{-1})	0.260	0.624
ΔB (dm^3 mol^{-1})	0.038	0.402

The *B*-coefficient of transfer from pure water (0.222 dm^3 mol^{-1}) to aqueous thiourea was calculated[30]. Values of Δ*B* (Table 2) are in line with the $\Delta_{tr}\varphi^0_v$ and therefore, it is concluded that the ion/charged-hydrophilic group interactions are much stronger and dominates over the ion-hydrophobic group interactions[30]. Glycine showed preference for contact with water than thiourea and its hydrogen bond sites get solvated by water rather than thiourea. Therefore, glycine-thiourea interactions are weaker than glycine-water.

CONCLUSION

Partial molar volumes (φ_v), partial molar volume of transfer ($\Delta_{tr}\varphi^0_v$) and viscosity *B*-coefficients of glycine + aqueous-thiourea solutions of 0.5 and 1.5 mol·dm^{-3} were determined at 298.15 K. Strong solute-solvent interactions strengthening with thiourea concentration and hydrophilic-hydrophilic as well as ion-hydrophilic or ion-polar interactions were observed in the studied systems. The φ^0_v was found to increase with increase in concentration of thiourea. Standard transfer volume of glycine, $\Delta_{tr}\varphi^0_v$ from pure water to aqueous thiourea solutions indicated that the hydrophilic-hydrophilic and ion-hydrophilic interactions exist in studied solutions. The dependence of ΔB over concentration of co-solute is in line with the results obtained for the $\Delta_{tr}\varphi^0_v$. Ion/charged-hydrophilic group interactions are stronger and dominates over the ion-hydrophobic group interactions. Strong solute-solvent interactions strengthening with concentration of thiourea were observed.

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