Study of Thermodynamic and Transport Properties of Glycine, Diglycine, and Triglycine in Aqueous Tartrazine at Different Temperatures

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The densities (ρ), viscosities (η), and refractive indices (n_D) of (0.01, 0.05, 0.10, 0.15, and 0.20 m) amino acid, glycine, and peptides, diglycine and triglycine in 0.01 m aqueous tartrazine solution were determined at 288.15, 293.15, 298.15, 303.15, 308.15, and 313.15 K. The density data were utilized to evaluate apparent molar volumes (ϕ_v) which, in turn, were used to determine partial molar volumes (ϕ_v°) using Masson's equation. The transfer volumes were also calculated. The viscosity data were analyzed using the Jones-Dole equation to determine the viscosity coefficients and the activation parameters. The activation parameters of viscous flow were obtained to throw light on the mechanism of viscous flow. The molar refraction was calculated using the refractive index data. The results were interpreted in the light of ion-ion, ion-nonpolar, and nonpolar-nonpolar interactions and the effect of increasing hydrophobicity as we move from glycine to triglycine on these interactions in presence of the dye tartrazine was also investigated.

Key words: Amino Acid; Peptides; Tartrazine; Partial Molar Volume; Viscosity *A*- and *B*-coefficients; Interactions.

1. Introduction

Macromolecules such as proteins, nucleic acids, and polysaccharides are evolutionary and prone to aqueous surroundings [1]. The structural units of proteins, such as amino acids, peptides, and their derivatives, are used as model compounds to study the conformational stability and behaviour of proteins in solutions.

The present work is a continuation of our program on the study of molecular interactions of amino acids/peptides in the presence of an additive tartrazine in aqueous medium from the measurement of various transport and thermodynamic properties [2 – 4]. Literature survey reveals that no studies have been carried out on these systems from the viewpoint of their thermodynamic and transport behaviours.

Azo colourants, such as tartrazine (E102), sunset yellow (E110), and allura red (E129), constitute one of the major synthetic colourant groups, used commercially in food, drinks, medicines, and cosmetics [5]. The dyes are widely used due to an inexpensive production and a large colour spectrum that can be obtained, when compared with natural colourants [6]. However, inspite of its commercial use, tartrazine is reported to catalyze hyperactivity [7], asthma [8, 9], migraines, thyroid cancer [10], and other behavioural problems [11].

Thus, keeping these considerations, experimentally measured densities (ρ), viscosities (η), and refractive indices (n_D) of aqueous tartrazine (0.01 m) and of solutions of glycine, diglycine, and triglycine (0.01, 0.05, 0.10, 0.15, and 0.20 m) in aqueous tartrazine at 288.15, 293.15, 298.15, 303.15, 308.15, and 313.15 K are presented. The parameters like apparent molar volume (ϕ_v), partial molar volume (ϕ_v°) and its experimental slope (S_v^*), transfer volume ($\phi_v^{\circ}{}_{(tr)}$), viscosity *A*- and *B*-coefficients, free energies of activation per mole of solvent ($\Delta\mu_1^{\circ *}$) and solute ($\Delta\mu_2^{\circ *}$), enthalpies (ΔH^*) and entropies (ΔS^*) of activation of viscous flow, and molar refraction (R_D) were calculated for all the amino acid/peptides in aqueous tartrazine solution from the experimental density, viscosity, and refractive index data. These parameters were discussed in terms of ion-ion, ion-nonpolar, and nonpolar-nonpolar interactions in the above mentioned mixtures.

2. Experimental

Glycine (E. Merck, Germany, mass fraction 0.99), diglycine (Acros organics, Belgium, mass fraction 0.99), and triglycine (Sigma, mass fraction 0.99)

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Table 1. Values of densities ρ, viscosities η, refractive indices n_D, of glycine, diglycine, and triglycine in aqueous tartrazine at different temperatures.

m	T (K)					
(mol kg^{-1})	288.15	293.15	298.15	303.15	308.15	313.15
Gly + aq. Tartrazine						
ρ (g cm^{-3})						
0.00	1.0023	1.0009	0.9994	0.9980	0.9966	0.9952
0.01	1.0028	1.0013	0.9997	0.9982	0.9967	0.9952
0.05	1.0042	1.0025	1.0008	0.9992	0.9976	0.9960
0.10	1.0057	1.0039	1.0022	1.0005	0.9988	0.9971
0.15	1.0072	1.0054	1.0036	1.0019	1.0001	0.9983
0.20	1.0087	1.0069	1.0051	1.0033	1.0015	0.9996
$10^3 \cdot \eta$ (N m^{-2} s)						
0.00	1.2105	1.0613	0.9357	0.8353	0.7526	0.6833
0.01	1.2134	1.0631	0.9367	0.8358	0.7527	0.6833
0.05	1.2189	1.0670	0.9397	0.8381	0.7543	0.6843
0.10	1.2245	1.0716	0.9436	0.8413	0.7568	0.6865
0.15	1.2308	1.0768	0.9476	0.8447	0.7600	0.6893
0.20	1.2372	1.0820	0.9521	0.8485	0.7632	0.6923
n_D						
0.00	1.3558	1.3553	1.3548	1.3543	1.3538	1.3533
0.01	1.3559	1.3554	1.3549	1.3544	1.3538	1.3533
0.05	1.3566	1.3560	1.3554	1.3548	1.3543	1.3537
0.10	1.3576	1.3569	1.3563	1.3557	1.3551	1.3545
0.15	1.3584	1.3577	1.3571	1.3565	1.3559	1.3552
0.20	1.3591	1.3585	1.3579	1.3572	1.3566	1.3559
Digly + aq. Tartrazine						
ρ (g cm^{-3})						
0.00	1.0023	1.0009	0.9994	0.9980	0.9966	0.9952
0.01	1.0028	1.0013	0.9997	0.9982	0.9967	0.9952
0.05	1.0053	1.0037	1.0020	1.0004	0.9988	0.9972
0.10	1.0087	1.0070	1.0052	1.0035	1.0017	1.0000
0.15	1.0116	1.0099	1.0081	1.0063	1.0045	1.0028
0.20	1.0145	1.0127	1.0109	1.0091	1.0073	1.0055
$10^3 \cdot \eta$ (N m^{-2} s)						
0.00	1.2105	1.0613	0.9357	0.8353	0.7526	0.6833
0.01	1.2138	1.0635	0.9373	0.8364	0.7531	0.6833
0.05	1.2220	1.0701	0.9426	0.8406	0.7568	0.6864
0.10	1.2327	1.0790	0.9500	0.8471	0.7622	0.6910
0.15	1.2453	1.0897	0.9594	0.8552	0.7692	0.6971
0.20	1.2579	1.1004	0.9687	0.8635	0.7768	0.7037
n_D						
0.00	1.3558	1.3553	1.3548	1.3543	1.3538	1.3533
0.01	1.3561	1.3556	1.3552	1.3545	1.3540	1.3536
0.05	1.3577	1.3573	1.3568	1.3563	1.3558	1.3553
0.10	1.3602	1.3597	1.3592	1.3587	1.3582	1.3576
0.15	1.3625	1.3620	1.3616	1.3610	1.3605	1.3599
0.20	1.3649	1.3644	1.3640	1.3634	1.3629	1.3623
Trigly + aq. Tartrazine						
ρ (g cm^{-3})						
0.00	1.0023	1.0009	0.9994	0.9980	0.9966	0.9952
0.01	1.0029	1.0014	0.9998	0.9983	0.9968	0.9953
0.05	1.0059	1.0043	1.0026	1.0011	0.9995	0.9979
0.10	1.0096	1.0080	1.0063	1.0046	1.0030	1.0013
0.15	1.0135	1.0118	1.0101	1.0084	1.0067	1.0050
0.20	1.0172	1.0155	1.0138	1.0122	1.0105	1.0087
$10^3 \cdot \eta$ (N m^{-2} s)						
0.00	1.2105	1.0613	0.9357	0.8353	0.7526	0.6833
0.01	1.2242	1.0721	0.9444	0.8423	0.7581	0.6876
0.05	1.2497	1.0935	0.9621	0.8571	0.7703	0.6980
0.10	1.2723	1.1127	0.9789	0.8714	0.7825	0.7085
0.15	1.2938	1.1309	0.9941	0.8848	0.7941	0.7189
0.20	1.3144	1.1486	1.0094	0.8974	0.8054	0.7289
n_D						
0.00	1.3558	1.3553	1.3548	1.3543	1.3538	1.3533
0.01	1.3568	1.3565	1.3563	1.3560	1.3556	1.3550
0.05	1.3600	1.3598	1.3595	1.3592	1.3589	1.3586
0.10	1.3638	1.3635	1.3631	1.3628	1.3625	1.3621
0.15	1.3670	1.3666	1.3664	1.3660	1.3657	1.3653
0.20	1.3705	1.3701	1.3697	1.3693	1.3688	1.3683

were used after recrystallization from ethanol/water mixtures and dried in vacuum over P_2O_5 at r. t. for 72 h before use. Analytical reagent grade, tartrazine (E. Merck, Germany, mass fraction 0.98) was used as such without further purification. Doubly distilled and deionized water was utilized for preparing 0.01 m aqueous tartrazine solution and was used as solvent to prepare 0.01, 0.05, 0.10, 0.15, and 0.20 m glycine, diglycine, and triglycine solutions. All the solutions were prepared by weight (molality basis) and weighings were done on Swiss-made electronic balance, Precisa XB-220A, with a precision of ± 0.0001 g. The solutions were stored in special air tight bottles to avoid contamination and evaporation.

The pycnometer and Ubbelohde-type suspended level viscometer were used for the density and viscosity measurements, respectively. The methodology is described in our earlier papers [2, 12]. Refractive indices were measured using thermostated Abbe refractometer after calibrating it with double distilled water and toluene at known temperatures. The accuracy in density, viscosity, and refractive index measurements was found to be ± 0.1 kg m^{-3}, $\pm 3 \cdot 10^{-6}$ N s m^{-2}, and ± 0.0002, respectively.

For the measurements of density, viscosity, and refractive index, the temperature of the solutions was maintained in an electronically controlled water bath (Julabo, Germany) having a precision of ± 0.02 K.

3. Results and Discussion

The measured density, viscosity, and refractive index for 0.01m aqueous tartrazine and of 0.01, 0.05, 0.10, 0.15, and 0.20 m glycine, diglycine, and

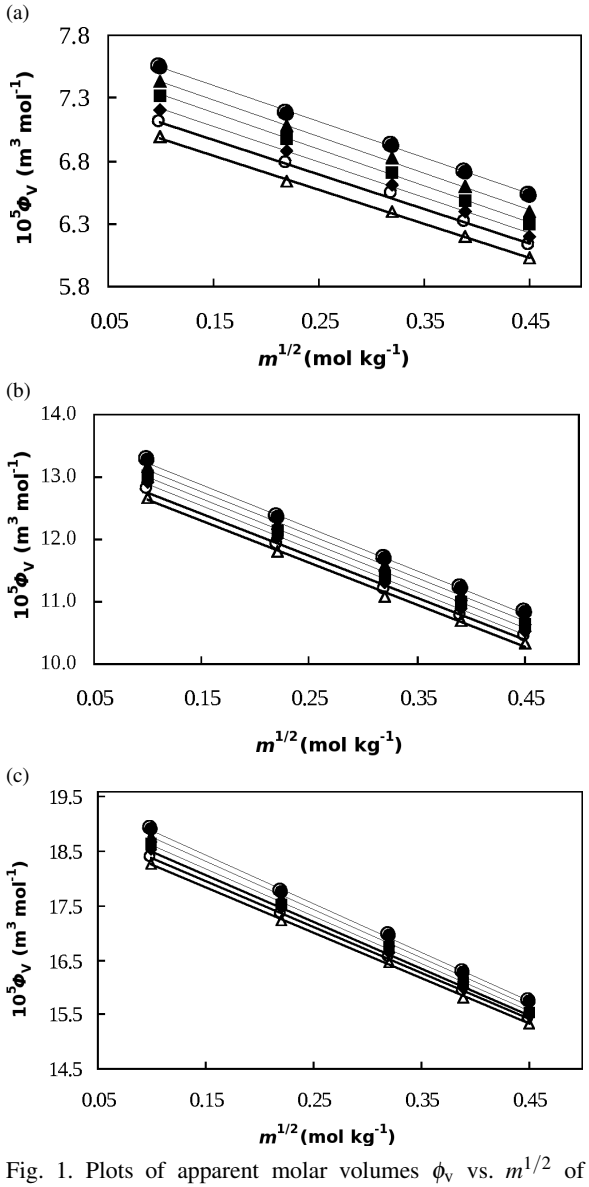

Fig. 1. Plots of apparent molar volumes ϕ_v vs. $m^{1/2}$ of (a) glycine; (b) diglycine; (c) triglycine in aqueous tartrazine at temperature T = {288.15 (△), 293.15 (○), 298.15 (◆), 303.15 (■), 308.15 (▲), 313.15 (●)} K

triglycine in aqueous tartrazine at 288.15, 293.15, 298.15, 303.15, 308.15, and 313.15 K are given in Table 1.

The apparent molar volumes of ternary solutions were determined from density data using the following relation:

$$\phi_v = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0}, \quad (1)$$

where M is the molecular weight of solute (glycine, diglycine, and triglycine) having molality m, ρ and ρ_0 are the densities of ternary solutions and solvent (aqueous tartrazine), respectively. The ϕ_v values of one amino acid (glycine) and two peptides (diglycine and triglycine) at the six temperatures are plotted against $m^{1/2}$ as shown in Figure 1. Figure 1 shows that ϕ_v is large positive for the amino acid/peptides in aqueous tartrazine solution, indicating the presence of strong solute-solvent interactions.

A valuable empirical generalization on the change of ϕ_v with square root of molal concentration is given by Masson's equation [13]:

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

where ϕ_v° is the partial molar volume that equals the standard partial molar volume or partial molar volume at infinite dilution and S_v^* is the experimental slope. At infinte dilution, m tends to 0, solute-solute interactions vanish, ϕ_v becomes equal to ϕ_v°, therefore, ϕ_v° gives an insight into the solute-solvent interactions. At finite dilution, S_v^* concerns with the solute-solute interactions. The ϕ_v° and S_v^* values are listed in Table 2.

In general, it is expected that the following types of interactions will take place in the mixtures:

(i) ion-ion interactions between zwitterions ($NH3^+$, COO^-) of amino acids / peptides and anions $SO^-{}_3$ / cations Na^+ of tartrazine ($C_{16}H_9N_4Na_3O_4S_2$).

(ii) ion-nonpolar group interactions between ($NH_3{}^+$, COO^-) of amino acid/peptides and hydrophobic group of tartrazine and between cations Na^+ / anions $SO^-{}_3$ of tartrazine and hydrophic part of amino acid/peptides.

(iii) nonpolar-nonpolar group interactions between hydrophobic side chains of amino acid/peptides and those of the dye, tartrazine.

Table 2 shows that the ϕ_v° values are found to increase from glycine to triglycine, which is due to the increase in the hydrophobicity of the alkyl chain. This points the dominance of interactions of type (ii) and (iii) over interactions of type (i).

The observed values of S_v^* (Table 2) are smaller than ϕ_v° values, implying the presence of weak solute-solute interactions. The negative values of S_v^* are due to the reduction in volume caused by ion-nonpolar and nonpolar-nonpolar group interactions. The S_v^* values are also found to decrease with rise in temperature for all amino acid/peptides, reflecting that the amino

Table 2. Values of ϕ_v°, $\phi_v^\circ{}_{(water)}$, $\phi_v^\circ{}_{(tr)}$, and $S_v{}^*$ of glycine, diglycine, and triglycine of aqueous tartrazine at different temperatures.

	T (K)					
	288.15	293.15	298.15	303.15	308.15	313.15
Gly + aq. Tartrazine						
$10^5 \cdot \phi_v^\circ$ ($m^3\,mol^{-1}$)	7.2583	7.3917	7.5106	7.6242	7.7341	7.8354
$10^5 \cdot S_v{}^*$ ($m^3\,dm^{1/2}\,mol^{-3/2}$)	−2.7447	−2.7910	−2.8920	−2.9372	−2.9500	−2.9158
$10^5 \cdot \phi_v^\circ{}_{(water)}$ ($m^3\,mol^{-1}$)	4.2480 [14]	—	4.3240 [15]	—	4.3790 [15]	4.4000 [16]
$10^5 \cdot \phi_v^\circ{}_{(tr)}$ ($m^3\,mol^{-1}$)	3.0103	—	3.1866	—	3.3551	3.4354
Diglycine + aq. Tartrazine						
$10^4 \cdot \phi_v^\circ$ ($m^3\,mol^{-1}$)	1.3328	1.3450	1.3583	1.3701	1.3824	1.3949
$10^5 \cdot S_v{}^*$ ($m^3\,dm^{1/2}\,mol^{-3/2}$)	−6.7976	−6.8522	−6.9551	−6.9772	−6.9899	−7.0450
$10^5 \cdot \phi_v^\circ{}_{(water)}$ ($m^3\,mol^{-1}$)	—	—	7.6280 [17]	—	7.7100 [17]	—
$10^5 \cdot \phi_v^\circ{}_{(tr)}$ ($m^3\,mol^{-1}$)	—	—	5.9546	—	6.1145	—
Trigly + aq. Tartrazine						
$10^4 \cdot \phi_v^\circ$ ($m^3\,mol^{-1}$)	1.9137	1.9272	1.9424	1.9552	1.9690	1.9822
$10^5 \cdot S_v{}^*$ ($m^3\,dm^{1/2}\,mol^{-3/2}$)	−8.5131	−8.6249	−8.8202	−8.9304	−9.0441	−9.1009
$10^4 \cdot \phi_v^\circ{}_{(water)}$ ($m^3\,mol^{-1}$)	—	—	1.1211 [18]	—	—	—
$10^5 \cdot \phi_v^\circ{}_{(tr)}$ ($m^3\,mol^{-1}$)	—	—	8.2129	—	—	—

acid/peptides act as structure-breakers in the present study.

The volumes of transfer ($\phi_v^\circ{}_{(tr)}$) for amino acid/peptides from aqueous to aqueous tartrazine solution were calculated using ϕ_v° data from the relation

$$\phi_v^\circ{}_{(tr)} = \phi_v^\circ \text{ (aq. tartrazine)} - \phi_v^\circ \text{ (aqueous)}. \quad (3)$$

The values of $\phi_v^\circ{}_{(tr)}$ are included in Table 2. The ϕ_v° (aq) were obtained from the literature [14–18]. It is evident from Table 2 that the values of ϕ_v° (aqueous tartrazine) are higher than ϕ_v° (aqueous), resulting in positive transfer volumes for all the amino acid/peptides. The increase in the volume of solutions in presence of tartrazine leads to the positive values of $\phi_v^\circ{}_{(tr)}$. This is due to the fact that amino acid/peptides under study induce a considerable contraction in volume of the peripheral solvent because of electrostriction [19]. This electrostrictive effect of amino acid/peptides is diminished on the addition of tartrazine due to the shielding effect of tartrazine molecules on the zwitterions. The structure of tartrazine shows the presence of several possible active sites that can interact with the zwitterions of amino acids/peptides. These active sites are a lone pair of electrons on two oxygen atoms and one on each nitrogen atom, which may interact with $NH^+{}_3$ of zwitterions glycine, diglycine, and triglycine. As a result, amino acid/peptides would not be able to exert the electrostriction effect at their maximum in the presence of dye tartrazine as compared to that in the pure water, thereby, resulting in a volume expansion and, hence, in positive transfer volumes. Similar conclusions were also drawn by others for amino acids in aqueous alkali chloride solutions [20] and in aqueous tetramethylammonium bromide solutions [21] and also by Ali et al. [22] for amino acids in aqueous caffeine solution.

The variation of relative viscosity (η_r) for amino acid/peptides in aqueous tartrazine solution can be represented by the Jones-Dole [23] equation:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm, \quad (4)$$

where η and η_0 are the respective viscosities of solution and solvent. A and B are the constants characteristic of ion-ion and ion-solvent interactions, respectively. A and B were obtained by the least-squares method as intercept and slope of the linear plots of $(\eta_r - 1)/m^{1/2}$ versus $m^{1/2}$.

Eyring and co-workers [24] proposed that the contribution per mole of solvent to the free energy of activation ($\Delta\mu_1{}^{0*}$) of viscous flow can be evaluated using the relation

$$\eta_0 = \left(\frac{hN_A}{\overline{V_1{}^0}}\right) \exp\left(\frac{\Delta\mu_1{}^{0*}}{RT}\right), \quad (5)$$

where h is the Planck constant, N_A the Avogadro's number, $\overline{V_1{}^0}$ the partial molar volume of solvent, R the universal gas constant, and T the temperature. The rearrangement of the above equation (5) gives:

$$\Delta\mu_1^{0*} = RT \ln\left(\frac{\eta_0 \overline{V_1{}^0}}{hN_A}\right). \quad (6)$$

According to Feakins et al. [25] the relation of B-coefficient to $\Delta\mu_2{}^{0*}$, the contributation per mole of solute (amino acid/peptides) to the free energy of activa-

Table 3. Values of Falkenhagen coefficient A, Jones-Dole coefficient B, free energy of activation per mole of solvent $\Delta\mu_1{}^{0*}$ and solute $\Delta\mu_2{}^{0*}$ of glycine, diglycine, and triglycine in aqueous tartrazine solution at different temperatures.

T (K)	A (10^2dm$^{3/2}$ mol$^{-1/2}$)	B (10^2dm^{3}mol^{-1})	$\Delta\mu_1{}^{0*}$ (kJ mol^{-1})	$\Delta\mu_2{}^{0*}$ (kJ mol^{-1})
Gly + aq. Tartrazine				
288.15	1.5100	7.3211	9.5896	26.5428
293.15	0.7663	7.7540	9.4388	27.4222
298.15	0.0986	8.3175	9.2913	28.4848
303.15	−0.3059	8.3487	9.1646	28.8504
308.15	−0.7640	8.4941	9.0521	29.3912
313.15	−1.0587	8.5752	8.9511	29.8486
Digly + aq. Tartrazine				
288.15	0.6521	17.391	9.5896	47.9623
293.15	−0.0032	17.761	9.4388	49.0829
298.15	−0.4128	17.820	9.2913	49.8103
303.15	−0.9203	18.187	9.1646	50.9763
308.15	−1.5057	18.669	9.0521	52.3448
313.15	−2.0619	18.895	8.9511	53.3819
Trigly + aq. Tartrazine				
288.15	9.0879	22.478	9.5896	62.4221
293.15	7.8700	23.523	9.4388	64.7016
298.15	6.9837	23.758	9.2913	65.9384
303.15	6.0214	23.893	9.1646	67.0434
308.15	4.9344	24.069	9.0521	68.2422
313.15	3.8661	24.743	8.9511	70.1676

tion of viscous flow is given by

$$B = \frac{1}{1000}\left[(\overline{V_1{}^0} - \overline{V_2{}^0}) + \frac{\overline{V_1{}^0}(\Delta\mu_2{}^{0*} - \Delta\mu_1{}^{0*})}{RT}\right], \quad (7)$$

where $\overline{V_2{}^0}$ ($= \phi_v{}^0$) is the partial molar volume of the solute. The rearrangement of (7) yields:

$$\Delta\mu_2{}^{0*} = \Delta\mu_1{}^{0*} + \frac{RT}{\overline{V_1{}^0}}[1000B - (\overline{V_1{}^0} - \overline{V_2{}^0})]. \quad (8)$$

The calculated values of A, B, $\Delta\mu_1^{0*}$, and $\Delta\mu_2^{0*}$ are summarized in Table 3.

It can be observed from Table 3 that the values of B-coefficients are higher as compared to A-coefficients, thereby supporting the behaviour of $\phi_v{}^\circ$ and $S_v{}^*$, respectively.

The sign of $(\partial B/\partial T)_P$ plays a crucial role in determining the structure-making/-breaking ability of solute rather than the size of B-coefficients [26]. The negative values of $(\partial B/\partial T)_P$ signify structure-making while positive values represent the structure-breaking ability of the solute. The variation of B with temperature is graphically shown in Figure 2. Figure 2 depicts that the sign of $(\partial B/\partial T)_P$ is positive for all the amino acids/peptides, suggesting that

Table 4. Values of enthalpies ΔH^*, entropies ΔS^*, and standard error of glycine, diglycine, and triglycine in aqueous tartrazine solution at different temperatures.

m (mol kg^{-1})	ΔH^* (kJ mol^{-1})	Std. Err.	ΔS^* (J mol^{-1} K^{-1})	Std. Err.
Gly + aq. Tartrazine				
0.00	0.1694	0.0031	0.0003	0.0000
0.01	0.0619	0.0343	−0.0010	0.0001
0.05	−0.3680	0.1825	−0.0063	0.0006
0.10	−0.9055	0.3678	−0.0128	0.0012
0.15	−1.4430	0.5531	−0.0193	0.0018
0.20	−1.9804	0.7384	−0.0258	0.0025
Digly + aq. Tartrazine				
0.00	0.1694	0.0031	0.0003	0.0000
0.01	0.0217	0.0277	−0.0019	0.0001
0.05	−0.5694	0.1292	−0.0106	0.0004
0.10	−1.3082	0.2562	−0.0215	0.0009
0.15	−2.0470	0.3831	−0.0324	0.0013
0.20	−2.7858	0.5101	−0.0432	0.0017
Trigly + aq. Tartrazine				
0.00	0.1694	0.0031	0.0003	0.0000
0.01	−0.0332	0.0529	−0.0026	0.0002
0.05	−0.8436	0.2672	−0.0142	0.0009
0.10	−1.8567	0.5351	−0.0286	0.0018
0.15	−2.8698	0.8030	−0.0430	0.0027
0.20	−3.8828	1.0709	−0.0574	0.0036

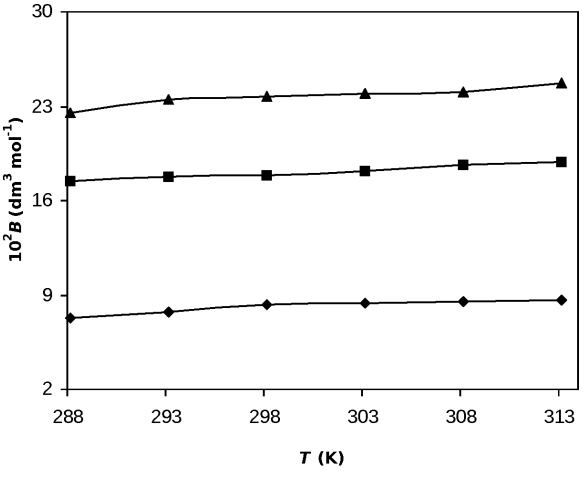

Fig. 2. Plots of B vs T of glycine (◆), diglycine (■), and triglycine (▲) in aqueous tartrazine at different temperatures.

all the amino acid/peptides studied are behaving as net structure-breakers in the presence of aqueous tartrazine. This supports the conclusions drawn by $S_v{}^*$ values.

A close perusal of Table 3 shows that the values of $\Delta\mu_2^{0*}$ are greater than $\Delta\mu_1^{0*}$ values, reflecting that the amino acid/peptide-solvent interaction in the ground state is stronger than in the transition state. The $\Delta\mu_2^{0*}$ values increase from glycine to triglycine im-

Table 5. Values of molar refractive index R_D of amino acids, glycine, diglycine, and triglycine in aqueous tartrazine at different temperatures.

m (mol kg^{-1})	$10^6 R_D$ (m^3 mol^{-1})					
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			Gly+ aq. Tartrazine			
0.00	3.9421	3.9426	3.9435	3.9441	3.9446	3.9451
0.01	3.9425	3.9434	3.9447	3.9456	3.9455	3.9464
0.05	3.9446	3.9453	3.9460	3.9463	3.9476	3.9480
0.10	3.9473	3.9479	3.9486	3.9493	3.9500	3.9508
0.15	3.9499	3.9505	3.9516	3.9523	3.9530	3.9536
0.20	3.9524	3.9531	3.9542	3.9547	3.9555	3.9560
			Diglycine+ aq. Tartrazine			
0.00	3.9421	3.9426	3.9435	3.9441	3.9446	3.9451
0.01	3.9434	3.9443	3.9466	3.9455	3.9464	3.9484
0.05	3.9503	3.9527	3.9544	3.9557	3.9570	3.9584
0.10	3.9629	3.9646	3.9667	3.9685	3.9706	3.9714
0.15	3.9753	3.9770	3.9802	3.9814	3.9835	3.9843
0.20	3.9886	3.9907	3.9939	3.9951	3.9973	3.9985
			Trigly+ aq. Tartrazine			
0.00	3.9421	3.9426	3.9435	3.9441	3.9446	3.9451
0.01	3.9500	3.9530	3.9573	3.9602	3.9622	3.9621
0.05	3.9713	3.9757	3.9794	3.9824	3.9858	3.9892
0.10	3.9960	3.9993	4.0021	4.0059	4.0094	4.0122
0.15	4.0137	4.0165	4.0213	4.0241	4.0279	4.0308
0.20	4.0349	4.0377	4.0406	4.0431	4.0450	4.0473

plying that as the hydrophobicity of the side chain of amino acid/peptides increases more energy is required in transferring the species from ground to transition state since more solute-solvent bonds are broken to attain the transition state. Similar results were also reported by Pal et al. [27] for amino acids in aqueous urea solutions.

The free energy of activation of viscous flow of solutions ($\Delta\mu^{0*}$) was determined using the equation

$$\Delta\mu^{0*} = n_1\Delta\mu_1{}^{0*} + n_2\Delta\mu_2{}^{0*}, \tag{9}$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively. The enthalpies (ΔH^*) and entropies (ΔS^*) of activation of viscous flow were calculated from the relation [27]

$$\Delta\mu^{0*} = \Delta H^* - T\Delta S^*. \tag{10}$$

The values of ΔH^* and ΔS^* are obtained from the linear plots of $\Delta\mu^*$ vs T, as intercept and slope, respectively. These parameters provide useful structural information about solute species and solute-solvent interactions. Their values are given in Table 4. It is observed from Table 4 that ΔH^* values decrease as the concentration of amino acid/peptides increases in the solution, indicating that the formation of the activated species required for viscous flow appears easy as the concentration of solute (amino acid/peptides) increases in the solution. The ΔS^* values are found to be negative

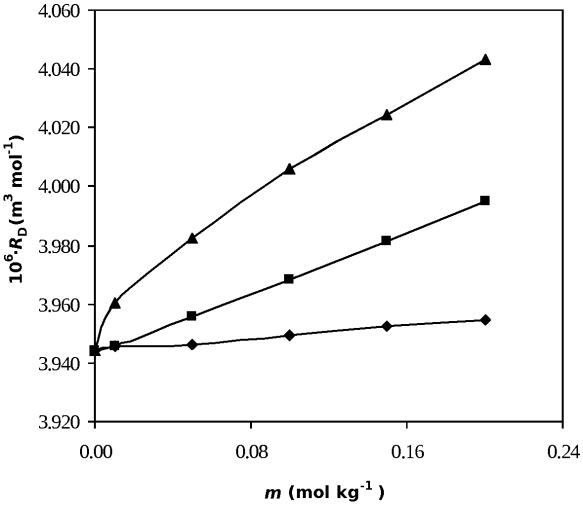

Fig. 3. Plots of R_D vs m of glycine (◆), diglycine (■), and triglycine (▲) in aqueous tartrazine at 303.15 K.

and show a pronounced decrease as the concentration of solute increases in the solutions, implying that the system is more structured during the viscous flow than it was in initial state, hence, indicating the presence of significant solute-solvent interactions in the system under investigation.

One of the most versatile tool to elucidate numerous physicochemical and thermophysical properties of multicomponent systems is the use of refractive index. It provides substantial information of the molecular in-

fluence on the intensity of the interactions in the mixtures.

The refractive index data are fitted into a Lorentz-Lorenz equation to calculate molar refractivity (R_D):

$$R_D = \frac{n_D^2 - 1}{n_D^2 + 2} \sum_{i=1}^{3} \frac{x_i M_i}{\rho}, \tag{11}$$

where x_i is the mole fraction of the i^{th} component of the mixture having molar mass M_i. The values of R_D at all investigated temperatures are summarized in Table 5 and plotted in Figure 3 as a functions of amino acid/peptides concentration. The variation of R_D with mixture composition gives information on the interaction in the mixtures [28]. Figure 3 shows that R_D increases almost linearly with increase in the amount of amino acid/peptides in aqueous tartrazine. Since R_D is directly proportional to molecular polarizability, Figure 3 exhibits an increase in overall polarizability of all the ternary systems under study with increasing amount of amino acid/peptides in the mixtures.

It is concluded that the volumetric, viscometric, and refractive index behaviours are in well agreement with each other.

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