

Interaction of Some Amino Acids with Sodium Dodecyl Sulphate in Aqueous Solution at Different Temperatures

Anwar Ali, Firdoos Ahmad Itoo, and Nizamul Haque Ansari

Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi – 110 025, India

Reprint requests to A. A.; E-mail: anwarali.chem@gmail.com

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The density ρ , and viscosity η of 0.00, 0.05, 0.10, 0.15, and 0.20 mol kg⁻¹ glycine (Gly), dl-alanine (Ala), dl-serine (Ser), and dl-valine (Val) have been measured in 0.002 mol kg⁻¹ aqueous sodium dodecyl sulphate (SDS) at 298.15, 303.15, 308.15, and 313.15 K. These data have been used to calculate the apparent molar volume ϕ_v , infinite dilution apparent molar volume ϕ_v° , and the standard partial molar volumes of transfer $\phi_{v(tr)}^\circ$, of the amino acids from water to the aqueous SDS solutions. Falkenhagen coefficient A , Jones-Dole coefficient B , free energies of activation per mole of solvent (aqueous SDS) $\Delta\mu_1^{\circ*}$, and per mole solute (amino acids) $\Delta\mu_2^{\circ*}$, also enthalpy ΔH^* and entropy ΔS^* of activation of viscous flow were evaluated using viscosity data. The molar refraction R_D was calculated by using experimental values of the refractive index n_D of the systems. The results have been interpreted in terms of ion-ion, ion-polar and hydrophobic-hydrophobic group interactions. The volume of the transfer data suggest that ion-ion interactions are predominant.

Key words: Density; Viscosity; Refractive Index; Amino Acids.

1. Introduction

The physico-chemical behaviour of proteins is strongly influenced by the presence of co-solutes. The presence of co-solutes markedly alter many properties of globular proteins, such as their hydration behaviour, solubility, stability, and conformations. However, due to the complex nature of proteins, direct investigations of the co-solute/solvent effect on these biological macromolecules are quite difficult [1]. It is, therefore, more convenient to study the physico-chemical properties of the building blocks of proteins, i. e., amino acids, in aqueous medium [1, 2]. Studies on the interaction of amino acids with surfactants can contribute towards an understanding of the surfactants as tools to isolate, solubilize, and manipulate membrane proteins for subsequent biochemical and physical characterization [3, 4]. In continuation of our studies on amino acid/surfactant interactions [5 – 7] using thermodynamic and transport properties, we intend to investigate interactions of glycine (Gly), dl-alanine (Ala), dl-serine (Ser), and dl-valine (Val) with sodium dodecyl sulphate (SDS) in aqueous medium at different temperatures. It has been reported that SDS acts as a more potent protein denaturant than urea and guanidine hydrochloride [8]. It is worth to mention that volu-

metric and viscometric properties have not been widely used in the biotechnological industry as is the case in the chemical industry. Moreover, volumetric and viscometric studies of amino acids in aqueous surfactants can provide valuable clues for understanding the protein unfolding [9] and about the hydrophobic interactions of non-polar side chains [1].

The above considerations led us to report the apparent molar volume ϕ_v , partial molar volume ϕ_v° , partial molar volume of transfer $\phi_{v(tr)}^\circ$, Falkenhagen and Jones-Dole viscosity coefficients, A and B , respectively, free energies of activation per mole of solvent $\Delta\mu_1^{\circ*}$ and per mole of solute $\Delta\mu_2^{\circ*}$, enthalpy ΔH^* and entropy ΔS^* of activation of viscous flow, and molar refractive index R_D evaluated by using measured values of density, viscosity, and refractive index of Gly, Ala, Ser, and Val in aqueous SDS solutions at different temperatures. Also, contributions of polar end groups (NH₃⁺, COO⁻), hydrophobic group –CH₂, and of –OH of amino acids to ϕ_v° were computed.

2. Experimental

The amino acids, viz. glycine (Merck, Purity > 99.0%), dl-alanine and dl-valine (Loba Chemie, Purities > 99%), dl-serine and sodium dodecyl sulphate

Table 1. Values of density ρ , viscosity η , and refractive indices n_D for glycine, dl-alanine, dl-serine, and dl-valine in aqueous SDS at different temperatures.

m (mol kg ⁻¹)	T (K)				m (mol kg ⁻¹)	T (K)			
	298.15	303.15	308.15	313.15		298.15	303.15	308.15	313.15
Glycine + 0.002 m aq. SDS					dl-Serine + 0.002 m aq. SDS				
	ρ (kg m ⁻³)					ρ (kg m ⁻³)			
0.00	1001.7	1000.0	998.4	996.7	0.00	1001.7	1000.0	998.4	996.7
0.05	1002.8	1001.0	999.3	997.5	0.05	1004.1	1002.3	1000.6	998.8
0.10	1004.4	1002.5	1000.7	998.8	0.10	1006.8	1004.9	1003.1	1001.3
0.15	1006.3	1004.3	1002.4	1000.4	0.15	1009.7	1007.8	1005.8	1003.8
0.20	1008.5	1006.5	1004.5	1002.3	0.20	1012.6	1010.6	1008.6	1006.6
	$10^3 \cdot \eta$ (N m ⁻² s)					$10^3 \cdot \eta$ (N m ⁻² s)			
0.00	0.8979	0.8042	0.7257	0.6590	0.00	0.8979	0.8042	0.7257	0.6590
0.05	0.9078	0.8147	0.7367	0.6704	0.05	0.9251	0.8313	0.7533	0.6860
0.10	0.9178	0.8244	0.7464	0.6793	0.10	0.9504	0.8556	0.7769	0.7092
0.15	0.9285	0.8347	0.7568	0.6888	0.15	0.9716	0.8789	0.7986	0.7303
0.20	0.9380	0.8449	0.7654	0.6968	0.20	0.9933	0.9001	0.8218	0.7506
	n_D					n_D			
0.00	1.3553	1.3529	1.3510	1.3495	0.00	1.3553	1.3529	1.3510	1.3495
0.05	1.3860	1.3140	1.3280	1.3150	0.05	1.3616	1.3602	1.3589	1.3580
0.10	1.3880	1.3250	1.3345	1.3255	0.10	1.3623	1.3612	1.3599	1.3600
0.15	1.3904	1.3470	1.3410	1.3280	0.15	1.3633	1.3620	1.3612	1.3608
0.20	1.3990	1.3580	1.3530	1.3315	0.20	1.3645	1.3635	1.3622	1.3614
dl-Alanine + 0.002 m aq. SDS					dl-Valine + 0.002 m aq. SDS				
	ρ (kg m ⁻³)					ρ (kg m ⁻³)			
0.00	1001.7	1000.0	998.4	996.7	0.00	1001.7	1000.0	998.4	996.7
0.05	1002.4	1000.6	998.9	997.1	0.05	1001.9	1000.1	998.4	996.6
0.10	1003.7	1001.7	999.9	998.0	0.10	1002.7	1000.8	999.0	997.1
0.15	1005.3	1003.2	1001.2	999.2	0.15	1003.9	1001.9	1000.0	998.0
0.20	1007.3	1004.8	1002.7	1000.6	0.20	1005.4	1003.3	1001.4	999.4
	$10^3 \cdot \eta$ (N m ⁻² s)					$10^3 \cdot \eta$ (N m ⁻² s)			
0.00	0.8979	0.8042	0.7257	0.6590	0.00	0.8979	0.8042	0.7257	0.6590
0.05	0.9440	0.8475	0.7676	0.6991	0.05	0.9529	0.8585	0.7798	0.7125
0.10	0.9685	0.8723	0.7909	0.7207	0.10	0.9854	0.8878	0.8084	0.7410
0.15	0.9902	0.8935	0.8106	0.7400	0.15	1.0165	0.9179	0.8352	0.7668
0.20	1.0105	0.9126	0.8318	0.7591	0.20	1.0422	0.9440	0.8597	0.7918
	n_D					n_D			
0.00	1.3553	1.3529	1.3510	1.3495	0.00	1.3553	1.3529	1.3510	1.3495
0.05	1.3261	1.3169	1.3155	1.3125	0.05	1.3600	1.3589	1.3589	1.3578
0.10	1.3340	1.3311	1.3275	1.3235	0.10	1.3603	1.3600	1.3601	1.3593
0.15	1.3471	1.3429	1.3399	1.3349	0.15	1.3629	1.3615	1.3615	1.3608
0.20	1.3517	1.3485	1.3462	1.3409	0.20	1.3638	1.3624	1.3624	1.3623

(Central Drug House, CDH, Pvt limited, Purities 98.5 and 99 %, respectively) were dried over P₂O₅ in vacuum desiccator before use. First stock solution of 0.002 m SDS was prepared in double distilled water and was used as a solvent to prepare 0.05, 0.10, 0.15, and 0.20 m solutions of all the amino acids. The weightings were done on an electronic balance (Precisa XB-220A, Swiss make) with a precision of ± 0.1 mg.

The density of the solutions were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of $8 \cdot 10^{-6}$ m³. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using double dis-

tilled water. The reproducibility of density measurements was within ± 0.01 kg m⁻³. The viscosities of the solutions were measured by using an Ubbelohde type suspended-level viscometer [10]. The viscometer was calibrated with double distilled water. The viscometer containing the test liquid was allowed to stand for about 30 minutes in a thermostated water bath so that the thermal fluctuations in the test solution were minimized. The times of flow were recorded with a digital stopwatch with an accuracy of ± 0.01 second. The viscosity data were reproducible within $\pm 3 \cdot 10^{-6}$ N s m⁻². The refractive indices of the solutions were measured by using a thermostated Abbe refractometer. The refractometer was calibrated by measuring the re-

fractive indices of double distilled water and toluene at the desired temperatures. The values of refractive index were obtained for sodium D light. The reproducibility of refractive index measurements was within ± 0.0001 . All the measurements were repeated at least three times for each sample and were found to be reproducible within the precision quoted for the apparatus. The temperature of the test solution during the measurements was maintained to an accuracy of ± 0.02 K in an electronically controlled thermostated water bath (JULABO, Model-MD, Germany).

3. Results and Discussion

The values of the apparent molar volume ϕ_v were calculated from the measured densities using the following equation:

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

where M is the molar mass of the solute (amino acid), m is its molality, ρ and ρ_0 are the densities of the solution (amino acids + SDS + water) ternary system and the solvent (aqueous SDS), respectively. The result of the density measurements at 298.15, 303.15, 308.15, and 313.15 K are given in Table 1. The values of ϕ_v of the amino acids in aqueous SDS at four studied temperatures are given in Table 2 and are plotted against $m^{1/2}$ (see Fig. 1). For each amino acid, ϕ_v vs $m^{1/2}$ plots were found to be linear in studied concentration range at all the four temperatures.

The value of standard partial molar volume ϕ_v° was obtained by least-squares fitting of ϕ_v to the following equation:

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

where ϕ_v° is the apparent molar volume of amino acid at infinite dilution, also known as the standard or simply partial molar volume of the solute. S_v^* is the slope which is also considered as the volumetric pairwise interaction coefficient [11]. ϕ_v° provides information regarding solute hydrophobicity, hydration properties, and solute-solvent interactions [1], whereas S_v^* provides information regarding solute-solute interactions. The values of ϕ_v° together with the values of S_v^* are given in Table 3. It is clear from the table that the ϕ_v° value increases as the size of hydrophobic alkyl group increases from Gly to Val at all four temperatures studied. The behaviour of amino acids in solution can be

Table 2. Values of apparent molar volumes ϕ_v for amino acids in aqueous SDS at different temperatures.

m (mol kg ⁻¹)	T (K)			
	298.15	303.15	308.15	313.15
$10^5 \cdot \phi_v$ (m ³ mol ⁻¹)				
Glycine + 0.002 m aq. SDS				
0.05	5.2959	5.5015	5.7081	5.9165
0.10	4.7905	4.9945	5.1997	5.4065
0.15	4.4177	4.6205	4.8245	5.0302
0.20	4.0781	4.2295	4.4322	4.6869
dl-Alanine + 0.002 m aq. SDS				
0.05	7.4934	7.7044	7.9161	8.1299
0.10	6.8869	7.1968	7.4073	7.6199
0.15	6.4787	6.7541	7.0309	7.2426
0.20	6.0694	6.4779	6.7374	6.9484
dl-Serine + 0.002 m aq. SDS				
0.05	5.6938	5.8954	6.0983	6.3027
0.10	5.3811	5.5816	5.7835	5.8861
0.15	5.1349	5.2679	5.5357	5.7382
0.20	5.0052	5.1544	5.3548	5.5063
dl-Valine + 0.002 m aq. SDS				
0.05	11.2942	11.5138	11.7338	11.9563
0.10	10.6878	10.9063	11.1252	11.3466
0.15	10.2110	10.4285	10.6466	10.8672
0.20	9.8151	10.0319	10.1983	10.3668

examined by considering the various possible interactions:

(i) The terminal charged groups, NH_3^+ and COO^- of zwitterions of amino acids, are hydrated in an electrostatic manner, while the hydration of intervening backbone depends on its nature, hydrophobic in case of Gly, Ala, and Val and H-bonding in case of Ser due to its $-\text{OH}$ group.

(ii) Electrostriction of the NH_3^+ group is about 10 times greater than of the COO^- group [12]. The overlap of hydration shells of terminal NH_3^+ and COO^- groups and of adjacent groups results in volume change.

The reduction in electrostriction at the terminals causes an increase in ϕ_v° whereas it decreases due to disruption of the side group hydration by that of the charged end. A marked increase in ϕ_v° in the sequence: Ser < Gly < Ala < Val (Table 3) is attributed to the increased hydrophobicity of the side chains of amino acids studied, as Ser contains polar $-\text{OH}$ side group, while the H-atom in Gly is replaced by a hydrophobic $-\text{CH}_3$ group in Ala and by a more hydrophobic $-\text{CH}(\text{CH}_3)_2$ group in Val. Out of the four amino acids investigated, only Ser has a polar side group in addition to polar-charged terminals, thereby causing a maximum contraction in volume followed by Gly with relatively freer N-terminal then by Ala and at least by

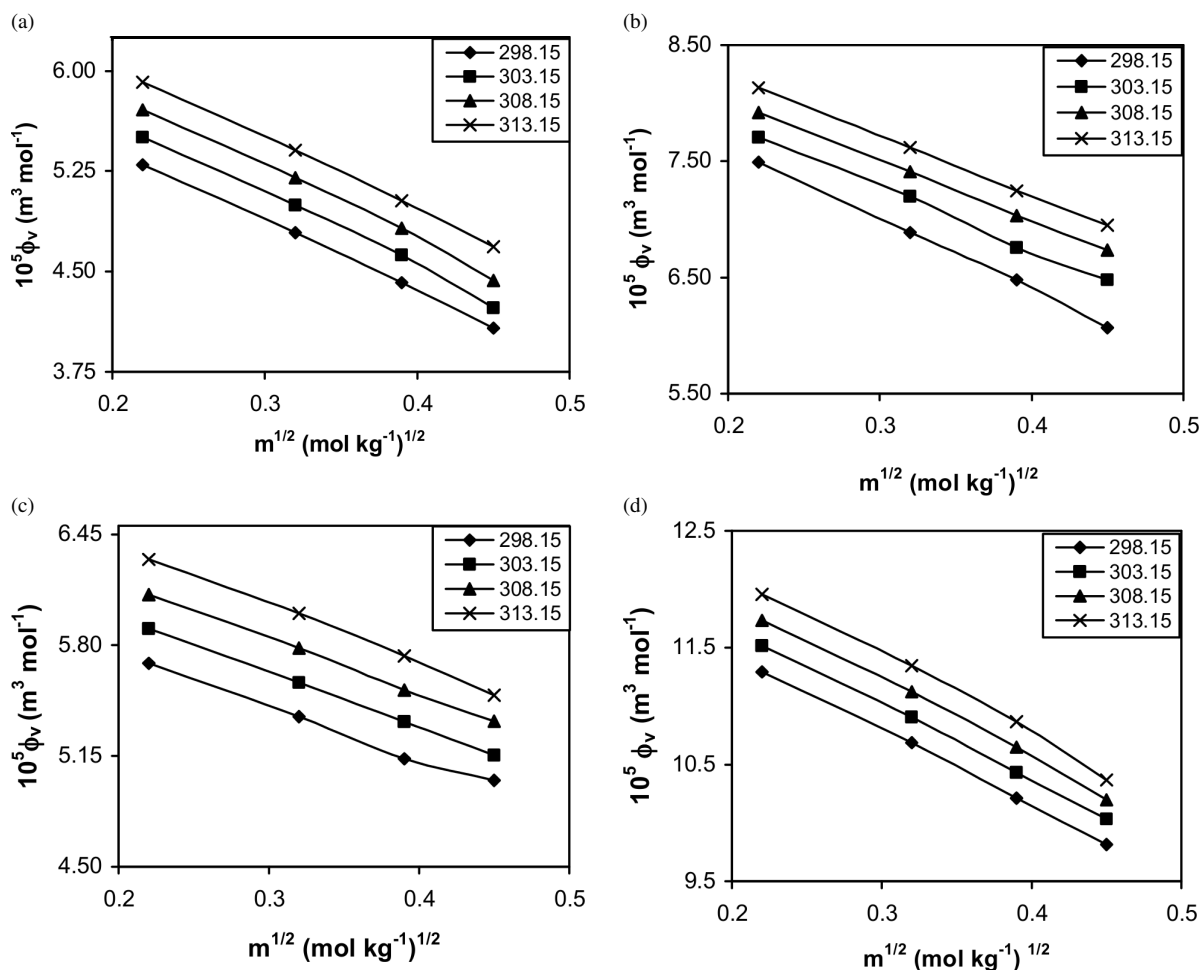


Fig. 1. Plots of apparent molar volume ϕ_v vs. $m^{1/2}$ of (a) glycine; (b) dl-alanine; (c) dl-serine; (d) dl-valine in aqueous SDS at different temperatures.

Val in which the N-terminal is highly shielded for electrostriction. Similar increase in ϕ_v° due to the increased shielding of N-terminal by the side groups of amino acids and peptides were also reported by Iqbal and Mateeullah [12]. The increase in ϕ_v° with temperature may be due to the release of some solvent molecules from the loose solvation layers to the bulk of the solution [13]. The values of S_v^* (Table 3) are negative for all the amino acids studied at all the four temperatures, indicating weak solute-solute interaction in aqueous SDS solution.

The partial molar thermodynamic properties of transfer provide qualitative as well as quantitative information regarding solute/co-solvent interaction [14]. The partial molar volume of transfer of amino acids from water to aqueous SDS, $\phi_{v(tr)}^\circ$, are calcu-

lated by using the relation

$$\phi_{v(tr)}^\circ(\text{water} \rightarrow \text{aq. SDS}) = \phi_{v(aq. SDS)}^\circ - \phi_{v(water)}^\circ \quad (3)$$

where $\phi_{v(water)}^\circ$ is the partial molar volume of amino acids in water and its values at 298.15 and 308.15 K have been taken from the literature [2, 15]. The $\phi_{v(tr)}^\circ$ values are summarized in Table 3. The following types of interactions are expected to occur in the ternary systems of amino acids in aqueous SDS:

a) Ion-ion interaction between SO_4^{2-} of SDS and NH_3^+ of amino acids, between the Na^+ ions of SDS and carboxylate anion COO^- of amino acids.

b) Ion-hydrophilic interaction between Na^+ of SDS and polar $-\text{OH}$ group of Ser.

Table 3. Values of ϕ_v° , $\phi_{v(tr)}^\circ$, and S_v^* for glycine, dl-alanine, dl-serine, and dl-valine in aqueous SDS at different temperatures.

	T (K)			
	298.15	303.15	308.15	313.15
Glycine + 0.002 m aq. SDS				
$10^5 \cdot \phi_v^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	6.5093	6.7706	6.9812	7.1417
$10^5 \cdot S_v^*$ ($\text{m}^3 \text{mol}^{-3/2} \text{kg}^{1/2}$)	-5.4243	-5.6293	-5.6466	-5.4764
$10^5 \cdot \phi_{v(aq)}^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	4.3240 [2]	—	4.3790 [15]	—
$10^5 \cdot \phi_{v(tr)}^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	2.1853	—	2.6022	—
dl-Alanine + 0.002 m aq. SDS				
$10^5 \cdot \phi_v^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	8.8995	8.9463	9.0893	9.3059
$10^5 \cdot S_v^*$ ($\text{m}^3 \text{mol}^{-3/2} \text{kg}^{1/2}$)	-6.3080	-5.5679	-5.2864	-5.2990
$10^5 \cdot \phi_{v(aq)}^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	6.0490 [2]	—	6.1010 [15]	—
$10^5 \cdot \phi_{v(tr)}^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	2.8505	—	2.9883	—
dl-Serine + 0.002 m aq. SDS				
$10^5 \cdot \phi_v^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	6.3822	6.6572	6.8431	7.0427
$10^5 \cdot S_v^*$ ($\text{m}^3 \text{mol}^{-3/2} \text{kg}^{1/2}$)	-3.1387	-3.4412	-3.3473	-3.4471
$10^5 \cdot \phi_{v(aq)}^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	6.0600 [15]	—	6.1150 [15]	—
$10^5 \cdot \phi_{v(tr)}^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	0.3222	—	0.7281	—
dl-Valine + 0.002 m aq. SDS				
$10^5 \cdot \phi_v^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	12.7770	13.0000	13.2750	13.5530
$10^5 \cdot S_v^*$ ($\text{m}^3 \text{mol}^{-3/2} \text{kg}^{1/2}$)	-6.6216	-6.6344	-6.8357	-7.0395
$10^5 \cdot \phi_{v(aq)}^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	9.0980 [15]	—	9.1550 [15]	—
$10^5 \cdot \phi_{v(tr)}^\circ$ ($\text{m}^3 \text{mol}^{-1}$)	3.6790	—	4.1200	—

c) Hydrophobic-hydrophobic interaction between the non-polar part of SDS and of amino acids.

d) Hydrophilic-hydrophobic interaction between —OH group of Ser and non-polar group of SDS.

Now taking the co-sphere overlap model [16] as a guide line according to which the effect of overlap of two co-spheres is destructive. Further, Mishra and Ahluwalia [17] extend this model and observed that overlapping of co-spheres of two ionic species relaxes some solvation water molecules to bulk so that overall the structure is increased, resulting in a volume increase. Whereas overlapping of co-spheres of hydrophilic-hydrophobic and hydrophobic-hydrophobic groups results in a net volume decrease. Thus, (a) and (b) types of interactions would lead to an increase in $\phi_{v(tr)}^\circ$ because of the reduction in electrostriction of water molecules due to the charged end groups (NH_3^+ , COO^-) of amino acids. This is due to the fact that interactions of these charged end groups of amino acids with SO_4^{2-} and Na^+ ions of SDS partially shield the electrostriction of the water molecules by these charged end groups of the amino acids. On the other hand, interactions of the types (c) and (d) yield negative $\phi_{v(tr)}^\circ$ values because of the weakening of the hydrogen-bonded structure of water around non-polar groups of SDS and amino acids. The observed positive $\phi_{v(tr)}^\circ$ values (Table 3) at both 298.15 and 308.15 K suggest that the interactions of the type (a) and (b)

Table 4. Contributions to ϕ_v° from the zwitterionic groups $\phi_v^\circ(\text{NH}_3^+, \text{COO}^-)$, the other alkyl groups $\phi_v^\circ(\text{R})$ ($\text{R} = -\text{CH}$, $-\text{CH}_2$, $-\text{CH}_3$, $-\text{CH}_3\text{CH}$, and $-(\text{CH}_3)_2\text{CHCH}$) and —OH group of amino acids at different temperatures.

	T (K)			
	298.15	303.15	308.15	313.15
	$10^5 \cdot \phi_v^\circ$ ($\text{m}^3 \text{mol}^{-1}$)			
$\text{NH}_3^+, \text{COO}^-$	3.714	3.924	4.063	4.190
—CH	1.095	1.093	1.107	1.126
—CH ₂	2.190	2.186	2.214	2.253
—CH ₃	3.285	3.279	3.322	3.380
—CH CH ₃	4.380	4.373	4.430	4.506
—CHCH (CH ₃) ₂	8.760	8.745	8.860	9.013
—OH	1.911	1.996	2.004	2.139
—CH CH ₂ OH	5.196	5.276	5.327	5.519

dominate over the (c) and (d) interactions in the present solutions of amino acids in aqueous SDS.

The values of ϕ_v° were least-squares fitted to the following equation in order to get the contributions of (NH_3^+ , COO^-) and (CH_2) group to ϕ_v° :

$$\phi_v^\circ = \phi_v^\circ(\text{NH}_3^+, \text{COO}^-) + n_c \phi_v^\circ(\text{CH}_2), \quad (4)$$

where n_c is the number of carbon atoms in the alkyl chain of the amino acids, $\phi_v^\circ(\text{NH}_3^+, \text{COO}^-)$ and $\phi_v^\circ(\text{CH}_2)$ are the zwitterionic end groups and the methylene group contributions to ϕ_v° , respectively. The values of $\phi_v^\circ(\text{NH}_3^+, \text{COO}^-)$ and $\phi_v^\circ(\text{CH}_2)$ are listed in Table 4. The value thus obtained for $\phi_v^\circ(\text{CH}_2)$ characterizes the mean contribution of —CH

Table 5. Values of Falkenhagen coefficients A , Jones-Dole coefficients B , free energies of activation per mole of solvent $\Delta\mu_1^{0*}$ and solute $\Delta\mu_2^{0*}$ of glycine, dl-alanine, dl-serine, and dl-valine in aqueous SDS at different temperatures.

	T (K)			
	298.15	303.15	308.15	313.15
Glycine + 0.002 m aq. SDS				
$10^2 \cdot A$ (dm ^{3/2} mol ^{-1/2})	-0.1705	0.2728	1.2902	2.5466
$10 \cdot B$ (dm ³ mol ⁻¹)	2.2829	2.4566	2.4729	2.3142
$\Delta\mu_1^{0*}$ (kJ mol ⁻¹)	9.1719	9.0523	8.9425	8.8409
$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)	47.1428	50.3860	51.4178	49.8716
dl-Alanine + 0.002 m aq. SDS				
$10^2 \cdot A$ (dm ^{3/2} mol ^{-1/2})	17.8277	18.0393	19.0013	20.2958
$10 \cdot B$ (dm ³ mol ⁻¹)	2.2632	2.7224	2.9907	3.0086
$\Delta\mu_1^{0*}$ (kJ mol ⁻¹)	9.1719	9.0480	8.9340	8.8279
$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)	50.1659	57.2320	61.9404	63.2672
dl-Serine + 0.002 m aq. SDS				
$10^2 \cdot A$ (dm ^{3/2} mol ^{-1/2})	3.6928	3.4904	4.5470	5.7573
$10 \cdot B$ (dm ³ mol ⁻¹)	4.5262	5.2286	5.5803	5.7051
$\Delta\mu_1^{0*}$ (kJ mol ⁻¹)	9.1719	9.0480	8.9340	8.8279
$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)	77.8963	89.1563	95.6406	99.0373
dl-Valine + 0.002 m aq. SDS				
$10^2 \cdot A$ (dm ^{3/2} mol ^{-1/2})	18.6770	21.0000	25.0320	27.3870
$10 \cdot B$ (dm ³ mol ⁻¹)	3.8953	3.9571	3.5981	3.8902
$\Delta\mu_1^{0*}$ (kJ mol ⁻¹)	9.1719	9.0480	8.9340	8.8279
$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)	78.0145	80.2234	76.5599	82.1828

and $-\text{CH}_3$ groups to ϕ_v° of the amino acids. Thus, the contributions due to the remaining portions, $-\text{CH}_2$ (Gly), $-\text{CH}_3\text{CH}$ (Ala), $-\text{CH}_3\text{CH}_2\text{CHCH}$ (Val), and $-\text{CHCH}_2\text{OH}$ (Ser) other than due to $(\text{NH}_3^+, \text{COO}^-)$ of amino acids were obtained by using the followings procedure suggested by Hakin et al. [18, 19]:

$$\phi_v^\circ(\text{CH}_3) = 1.5 \phi_v^\circ(\text{CH}_2), \quad (5)$$

$$\phi_v^\circ(\text{CH}) = 0.5 \phi_v^\circ(\text{CH}_2), \quad (6)$$

$$\begin{aligned} \phi_v^\circ(\text{OH}) &= \phi_v^\circ(\text{Ser}) - \phi_v^\circ(\text{NH}_3^+, \text{COO}^-) \\ &\quad - \phi_v^\circ(\text{CH}_2) - \phi_v^\circ(\text{CH}). \end{aligned} \quad (7)$$

These contributions to ϕ_v° are also included in Table 4. It is clear from the table that contribution due to hydrophobic moieties of the amino acids to ϕ_v° follow the sequence: $-\text{CH}_2 < -\text{CH}_3\text{CH} < -\text{CH}_3\text{CH}_2\text{CHCH}$. This again supports the view that ϕ_v° increases as the hydrophobic character of the amino acid molecule increases from Gly to Val.

The viscosity A - and B -coefficients of amino acids in aqueous SDS were analysed by using the Jones-Dole [20] equation:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm, \quad (8)$$

where $\eta_r \left(= \frac{\eta}{\eta_0} \right)$ is the relative viscosity of the solution, η and η_0 are the viscosities of the solution and

solvent (aqueous SDS), respectively. The values of viscosities of solvent and solution are presented in Table 1 along with the density and refractive index data as a function of amino acids concentration and temperature. A and B are Falkenhagen [21] and Jones-Dole [20] coefficients, respectively. The coefficient A reflects the solute-solute, while B reflects solute-solvent interactions. In general, positive B -coefficients suggest cosmotrops since strongly hydrated solutes exhibit a large change in viscosity with concentration, while negative B -coefficients indicate chaotropes for weakly hydrated solutes [1]. The values of A and B have been obtained from the intercepts and slopes of the plots $(\eta_r - 1)/m^{1/2}$ vs $m^{1/2}$ and are included in Table 5. From the table it is evident that the values of both A - and B -coefficients are positive, but the B -values are far greater than the A -values, particularly for Gly and Ser, which justifies that the solute-solvent interaction predominates over the solute-solute interaction and that out of the four amino acids studied, Gly and Ser are strongly hydrated as they have very large values of the B -coefficient as compared to Ala and Val which have relatively small B -values and, thus, are weakly hydrated. This clearly suggests that the solute-solvent interaction is greatly affected by the polarity of the solute. The viscosity data have also been examined in the light of the transition state theory of the relative viscosity proposed by Feakins et al. [21]. According to this theory the B -coefficient is given by

Table 6. Values of enthalpies ΔH^* and entropies ΔS^* of activation of viscous flow and molar refractive index R_D for glycine, dl-alanine, dl-serine and dl-valine in aqueous SDS at different temperatures.

m (mol kg ⁻¹)	ΔH^* (J mol ⁻¹)	ΔS^{**} (kJ mol ⁻¹ K ⁻¹)	$10^6 \cdot R_D$ (m ³ mol ⁻¹)			
			298.15 K	303.15 K	308.15 K	313.15 K
Glycine + 0.002 m aq. SDS						
0.00	0.0314	0.0000	3.9214	3.9041	3.8914	3.8830
0.05	-0.3008	0.0091	4.2396	3.5242	3.6732	3.5468
0.10	-0.6332	0.0184	4.2552	3.6342	3.7377	3.6539
0.15	-0.9656	0.0276	4.2760	3.8536	3.8010	3.6763
0.20	-1.2980	0.0368	4.3577	3.9618	3.9185	3.7088
dl-Alanine + 0.002 m aq. SDS						
0.00	0.0320	0.0000	3.9214	3.9041	3.8914	3.8830
0.05	-10.5128	0.0440	3.6266	3.5396	3.5313	3.5069
0.10	-21.0577	0.0880	3.7022	3.6804	3.6505	3.6168
0.15	-31.6025	0.1320	3.8280	3.7940	3.7715	3.7287
0.20	-41.1473	0.1760	3.8667	3.8445	3.8296	3.7845
dl-Serine + 0.002 m aq. SDS						
0.00	0.0320	0.0000	3.9214	3.9041	3.8914	3.8830
0.05	-16.8135	-0.0699	3.9751	3.9684	3.9623	3.9605
0.10	-33.6591	-0.1398	3.9722	3.9689	3.9632	3.9713
0.15	-50.5046	-0.2092	3.9715	3.9662	3.9662	3.9702
0.20	-67.3502	-0.2796	3.9727	3.9708	3.9659	3.9659
dl-Valine + 0.002 m aq. SDS						
0.00	0.0320	0.0000	3.9214	3.9041	3.8914	3.8830
0.05	1.2919	0.0088	3.9682	3.9644	3.9711	3.9674
0.10	2.5517	0.0176	3.9689	3.9735	3.9817	3.9813
0.15	3.8116	0.0265	3.9909	3.9850	3.9926	3.9936
0.20	5.0714	0.0353	3.9948	3.9893	3.9969	4.0039

the relation

$$B = \frac{(\bar{V}_1^0 - \bar{V}_2^0)}{1000} + \frac{\bar{V}_1^0 (\Delta\mu_2^{0*} - \Delta\mu_1^{0*})}{1000RT}, \quad (9)$$

where $\bar{V}_1^0$ and $\bar{V}_2^0 (= \phi_v^0)$ are the partial molar volumes of the solvent (aqueous SDS) and solute (amino acids), respectively. The free energy of activation per mole of solvent $\Delta\mu_1^{0*}$ has been calculated by using the following relation proposed by Glasstone et al. [22]:

$$\Delta\mu_1^{0*} = RT \ln \left(\frac{\eta_0 \bar{V}_1^0}{h N_A} \right), \quad (10)$$

where h and N_A are the Planck constant and the Avogadro number, respectively. The above equation rearranges to give free energies of activation per mole of the solute, $\Delta\mu_2^{0*}$:

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + \left(\frac{RT}{\bar{V}_1^0} \right) [1000B - \bar{V}_1^0 - \bar{V}_2^0]. \quad (11)$$

The values of $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ are also included in Table 5. It is evident that for the amino acids under study, the $\Delta\mu_2^{0*}$ -values are positive and much large

than those of $\Delta\mu_1^{0*}$ in aqueous SDS, suggesting that solute-solvent interactions are stronger in the ground state than in the transition state. Hence, the solvation of the solute (amino acids) in the transition state is less favoured in energy terms. Further, $\Delta\mu_2^{0*}$ increases markedly in the sequence Gly < Ala < Val at a given temperature, indicating that solvation of amino acids becomes increasingly unfavourable as the hydrophobicity of the side chain increases from Gly to Val. Serine has smaller $\Delta\mu_2^{0*}$ -values due to its polar side-group -OH. Thus, conclusions drawn from the $\Delta\mu_2^{0*}$ are in agreement with those drawn from the trends of ϕ_v^0 , S_v^* , and B -values.

The free energy of activation ΔG^* of viscous flow of the ternary solutions (amino acids + aqueous SDS) was obtained by using the equation given by Feakins and co-workers [23]:

$$\Delta G^* = n_1 \Delta\mu_1^{0*} + n_2 \Delta\mu_2^{0*}, \quad (12)$$

where n_1 and n_2 are the number of moles of the solvent (aqueous SDS) and solute (amino acid), respectively. Then, the entropy and enthalpy of activation of viscous flow were calculated by using the equation

$$\Delta G^* = \Delta H^* - T \Delta S^*. \quad (13)$$

ΔH^* and ΔS^* are obtained from intercepts and slope of the plots of ΔG^* vs T . The results are given in Table 6. It is clear from the table that there is a marked decrease in ΔH^* with an increase in the concentration of Gly, Ala and Val, while, the reverse is observed for Ser. This indicates that the formation of the activated species necessary for viscous flow seems to be easy as the amount of Gly, Ala, and Val increases in the solution while reverse is the case with Ser in aqueous SDS solution. The values of ΔS^* are found to increase with the increase in concentration of Gly, Ala, and Val, whereas an opposite trend is noticed for Ser, indicating that the system becomes less structured during the viscous flow than in the initial state in case of Gly, Ala, and Val but opposite is the case with Ser in aqueous SDS solution.

The experimental values of the refractive indices (Table 1) show an increasing trend with an increase in concentration of amino acids in the solution, indicating that the refractive index is influenced by the presence of interactions between the components in the solution. The refractive index data were used to calculate

the molar refraction R_D , by using the Lorentz-Lorenz equation

$$R_D = \frac{n_D^2 - 1}{n_D^2 + 1} \frac{\sum_{i=1}^3 x_i M_i}{\rho}, \quad (14)$$

where x_i and M_i are the mole fraction and molar mass of the i th component of the mixture. The values of R_D are included in Table 6. It indicates that the values of all the four amino acids increase with an increase in the concentration of the amino acids in the solution. Since R_D is directly proportional to the molecular polarizability, the overall polarizability of the systems under study increases with concentration of the amino acids in the solution. This is in good agreement with the results reported by Ali et al. [24] for amino acids in aqueous glucose.

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