

## Studies on DL-Serine in Water by Volumetric and Viscometric Measurement at T=(288.15, 295.15, 302.15, 309.15, and 316.15) K.

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**Abstract:** Density,  $\rho$  and viscosity,  $\eta$ , of DL-serine aqueous solutions have been determined at (288.15, 295.15, 302.15, 309.15, and 316.15) K. The measured values of density and viscosity have been used to estimate some important parameters, such as apparent molal volume,  $\phi_v$ , limiting apparent molal volume,  $\phi_v^0$ , experimental slope,  $S_v$ , second derivative of limiting apparent molal volume,  $\left[\partial^2 \phi_v^0 / \partial T^2\right]$ , viscosity A and B coefficients, free energy of activation,  $\Delta G^\ddagger$ , enthalpy of activation,  $\Delta H^\ddagger$ , entropy of activation,  $\Delta S^\ddagger$ .

**Keywords:** DL-serine, Apparent molar volume, activation parameters, viscosity A and B coefficients, solute-solute and solute-solvent interactions.

### I. Introduction

Proteins are the biomolecules, which play a vital role in all the biological processes occurring in living organisms. Their behavior can be governed by their interactions with the surrounding environment. The study of thermodynamic stability of the native structure of proteins has proved quite challenging and still remains a subject of extensive investigation [1]. Due to the complexities arising from direct thermodynamic study on proteins, investigations on the behavior of model compounds of proteins like amino acids and peptides in aqueous and mixed aqueous solvents make one to understand the factors governing the stability of the biopolymers [2, 3]. The interpretation of behavior of amino acids is quite helpful in understanding the water-protein interactions in solutions. Moreover volumetric and viscometric studies of amino acids in aqueous solutions can provide valuable information for understanding protein unfolding [4-7]. Mixed aqueous solvents are extensively used in chemistry and other fields to control factors like stability, reactivity and solubility of systems [8, 9]. In this paper, we present the volumetric and viscometric studies of DL-serine in aqueous solutions. Studies on densities and viscosities of amino acid solutions are of great use in characterizing the structure and properties of solutions. Various types of interactions exist between the solutes in solutions, and these solute-solute and solute-solvent interactions are of current interest in all branches of chemistry. These interactions provide a better understanding of the nature of the solute and solvent, i.e., whether the solute modifies or distorts the structure of the solvent. In the present work, we have reported that the values of density and viscosity have been measured for DL-serine in aqueous solution at T (288.15, 295.15, 302.15, 309.15, and 316.15) K. The relevant parameters which are related to our study such as apparent molal volume,  $\phi_v$ , limiting apparent molal volume,  $\phi_v^0$ , and its related constant,  $S_v$ , second derivative of limiting apparent molal volume,  $\left[\partial^2 \phi_v^0 / \partial T^2\right]$ , viscosity A and B coefficients, activation parameters [free energy,  $\Delta G^\ddagger$ , entropy,  $\Delta S^\ddagger$ , and enthalpy,  $\Delta H^\ddagger$ ], have been evaluated meticulously. All these parameters are used to discuss the solute-solute and solute-solvent interactions occurring in the binary DL-serine in water system as well as the structure making/breaking tendency of DL-serine in aqueous system.

### II. Experimental

The amino acid used in this study was DL-serine. DL-serine (purity, Mass fraction  $\geq 0.99$ ) procured from Fluka chemical company, Switzerland was used without further purification. Supplied distilled water was redistilled and deionized by passing through two ion exchange columns. The deionized water was distilled again in alkaline  $\text{KMnO}_4$  medium and used for preparation of solution.

Densities of DL-serine in aqueous solutions were measured using high precision vibrating tube digital density meter (DSA-5000 M, Anton Paar, Austria). The DSA-5000 M density is the world's most accurate density measurement. The accuracies in density were found to be  $0.000005 \text{ g}\cdot\text{cm}^{-3}$  respectively. The method is based on the principle of time lapse measurement for certain number of oscillations of a vibrating U-shaped sample tube filled with the sample liquid. The temperature of the sample tube is controlled by two integrated in-built 100  $\Omega$  Pt resistance thermometers to a level of highest accuracy and traceable to national standards. The temperature of the sample tube is controlled to  $\pm 0.001 \text{ K}$ . Viscosities of various liquids were measured using

calibrated Ostwald type viscometer. The flow time of liquids were recorded by a timer (stop-watch) capable to read up to 0.01 seconds. The temperature was controlled by water thermostat with an accuracy of ± 0.1 K. The solutions were prepared by weight immediately before the measurement. For the measurement of viscosity the interior of the viscometer was cleaned thoroughly with warm chromic acid and then with distilled water, so that there was no obstruction in the capillary and the liquid could run freely without leaving any drop behind.

### III. Results and Discussion

#### 1. Apparent molar volume

The measured densities,  $\rho$ , and the apparent molal volume,  $\varphi_v$ , of DL-Serine in aqueous solution are listed in table 1 to table 2 as functions of concentration and temperatures at (288.15, 295.15, 302.15, 309.15 and 316.15) K respectively. The apparent molar volumes,  $\varphi_v$ , of DL-Serine in binary solution are calculated from measurements density using the following equation

$$\varphi_v = \left[ \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \right] \quad (1)$$

where  $M$ ,  $m$  and  $\rho_0$  are molar mass, molality of solute (DL-Serine), and density of pure water respectively.

**Table 1:** Densities of water, ( $\rho^0$ ), aqueous DL-serine solutions, ( $\rho$ ), at T= (288.15, 295.15, 302.15, 309.15, and 316.15) K.

$m$ /mol·kg <sup>-1</sup>	$\rho$ /g·cm <sup>-3</sup>				
	288.15 K	295.15 K	302.15 K	309.15 K	316.15 K
0.0000	0.999157	0.997820	0.995993	0.993730	0.991082
0.0497	1.001392	1.000021	0.998166	0.995886	0.993221
0.1001	1.003633	1.002229	1.000348	0.998049	0.995361
0.1499	1.005818	1.004390	1.002483	1.000171	0.997462
0.2019	1.008093	1.006626	1.004697	1.002369	0.999645
0.2497	1.010162	1.008674	1.006725	1.004375	1.001626
0.2972	1.012206	1.010699	1.008721	1.006359	1.003595
0.3503	1.014447	1.012922	1.010930	1.008549	1.005754
0.4035	1.016667	1.015094	1.013105	1.010694	1.007892

**Table 2:** Apparent molal volume ( $\varphi_v$  /cm<sup>3</sup>·mol<sup>-1</sup>) of aqueous DL-serine solutions T= (288.15, 295.15, 302.15, 309.15, and 316.15) K.

$m$ /mol·kg <sup>-1</sup>	$\varphi_v$ /cm <sup>3</sup> ·mol <sup>-1</sup>				
	288.15 K	295.15 K	302.15 K	309.15 K	316.15 K
0.0497	60.04	60.75	61.35	61.73	62.13
0.1001	60.10	60.80	61.37	61.78	62.23
0.1499	60.25	60.88	61.45	61.83	62.29
0.2019	60.31	60.98	61.52	61.89	62.32
0.2497	60.36	60.99	61.52	61.91	62.37
0.2972	60.40	61.00	61.55	61.93	62.38
0.3503	60.53	61.10	61.61	61.99	62.47
0.4035	60.64	61.26	61.70	62.11	62.56

The apparent molar volume at infinite dilution,  $\varphi_v^0$ , is calculated using least square fit to the linear plots of experimental values of  $\varphi_v$  versus molal concentration,  $m$ , using the following Masson equation [10]

$$\varphi_v = \varphi_v^0 + S_v m \quad (2)$$

where  $S_v$  is the experimental slope, which is sometimes considered to be the volumetric pairwise interaction coefficient [11,12].  $S_v$  is a measure of solute-solute interactions. The limiting apparent molal volume,  $\varphi_v^0$  and  $S_v$  values are given in Table 3. It is evident from the Table 3 that the values of  $S_v$  are positive for DL-Serine in water at different temperatures. The result indicates the presence of very strong ion-ion interactions. The limiting apparent molal volume,  $\varphi_v^0$ , which is taken to be the partial molal volume at infinite dilution of DL-Serine in aqueous solutions reflect the true volume of the solute and the volume change arising from solute-solvent interactions. The variation of  $\varphi_v^0$  with the molality of DL-Serine can be rationalized in terms of cosphere overlap model [13]. According to the model, the overlap of the co-spheres of two ions or polar groups or an ion with that of hydrophilic groups always produces a positive volume change. On the other hand, the overlaps of the co-spheres of an ion with that of hydrophobic groups result in a negative volume change. The temperature dependence of limiting apparent molal volume,  $\varphi_v^0$ , for DL-Serine in aqueous solutions can be expressed by the following expression

$$\phi_v^0 = a + bT + cT^2 \quad (3)$$

The sign of  $[\partial^2 \phi_v^0 / \partial T^2]$  i.e. second derivative of limiting apparent molal volume of solution with respect to temperature at constant pressure which corresponds to structure making or breaking properties of solution were determined [14]. DL-serine in aqueous solutions systems show negative value of  $[\partial^2 \phi_v^0 / \partial T^2]$  which is represented in tables 3. The negative volumes of  $[\partial^2 \phi_v^0 / \partial T^2]$  indicate that DL-serine act as a structure breaker for water solvent systems. Similar information was reported by Devine and Lowe [15].

**Table 3:** Limiting apparentmolal volume ( $\phi_v^0$ ) and experimental slopes ( $S_v$ ) for DL-Serine aqueous solutions at T= (288.15, 295.15, 302.15, 309.15, and 316.15) K.

T/ K	$\phi_v^0 / \text{cm}^3 \text{mol}^{-1}$	$S_v / \text{cm}^3 \text{lit}^{1/2} \text{mol}^{-1}$	$[\partial^2 \phi_v^0 / \partial T^2]_p$
288.15	59.96	1.67	-0.0012
295.15	60.68	1.33	
302.15	61.30	0.96	
309.15	61.68	1.00	
316.15	62.10	1.12	

## 2. Viscosity

Viscosities in aqueous DL-Serine have been determined at T (288.15, 295.15, 302.15, 309.15 and 316.15) K respectively. The relevant data are shown in table 4. The values of  $\eta$  increase with increase in molality and decrease with temperature. According to the ‘Flickering cluster’ [16] model of water, there are large void spaces within the hydrogen-bonded framework of water structure. The linear increase of  $\eta$  with concentration may be interpreted by the fact that the molecules may have penetrated in the void spaces and may have a positive interaction with water.

**Table 4:** Viscosities of water,  $\eta_0$ , DL-serine in aqueous solution,  $\eta$ , at T= (288.15, 295.15, 302.15, 309.15 and 316.15) K.

$m / (\text{mol} \cdot \text{kg}^{-1})$	$\eta / \text{cP}$				
	288.15 K	295.15 K	302.15 K	309.15 K	316.15 K
0.0000	1.1404	0.9579	0.8180	0.7085	0.6207
0.0497	1.1539	0.9679	0.8271	0.7164	0.6280
0.1001	1.1654	0.9772	0.8393	0.7235	0.6390
0.1499	1.1744	0.9900	0.8520	0.7331	0.6501
0.2019	1.1833	0.9959	0.8604	0.7420	0.6573
0.2497	1.2069	1.0075	0.8664	0.7482	0.6633
0.2972	1.2187	1.0219	0.8800	0.7570	0.6694
0.3503	1.2250	1.0357	0.8895	0.7651	0.6747
0.4035	1.2402	1.0511	0.9046	0.7715	0.6891

To calculate the B and D-coefficient values, the viscosity data have been analyzed in terms of the semi-empirical Jones-Dole equation arranging into straight line from given below [17]:

$$\frac{\eta}{\eta_0} = 1 + BC + DC^2$$

$$\text{or, } \frac{\eta_r - 1}{C} = B + DC \quad (4)$$

The B-coefficient represents the solute-solvent interaction and shape and size effect on the solvent structure [18-19]. The calculated values of the B and D-coefficient are represented in Table 8. For aqueous DL-serine solutions, the table 5 reports that the values of  $[dB/dT]$  have positive which corresponds to structure breaking behavior. The simplest amino acid DL-serine are classified as structure breaker, which supporting the behavior of  $S_v$ , and  $[\partial^2 \phi_v^0 / \partial T^2]$  respectively.

**Table 5:** The viscosity coefficient values of B, D and  $[dB/dT]$  for DL-serine aqueous solutions at T= (288.15, 295.15, 302.15, 309.15 and 316.15) K.

T/ K	B	D	$[dB/dT]$
288.15	0.2192	0.0036	0.0020
295.15	0.2119	0.0698	
302.15	0.2460	0.0506	
309.15	0.2244	0.0257	
316.15	0.2843	-0.0152	

The enthalpy of activation  $\Delta H_{\eta}^{\ddagger}$  and subsequently other thermodynamic parameter such the activation free energy,  $\Delta G_{\eta}^{\ddagger}$ , and entropy of activation,  $\Delta S_{\eta}^{\ddagger}$ , were calculated from the plot of  $\log \eta$  versus  $1/T$  using following relations:

$$\Delta G_{\eta}^{\ddagger} = RT \ln (\eta V_m / Nh) = \Delta H_{\eta}^{\ddagger} - T \Delta S_{\eta}^{\ddagger} \quad (5)$$

$$\text{or, } \Delta S_{\eta}^{\ddagger} = (\Delta H_{\eta}^{\ddagger} - \Delta G_{\eta}^{\ddagger}) / T$$

Therefore,

$$\Delta S_{\eta}^{\ddagger} = \Delta H_{\eta}^{\ddagger} / T + R \ln (\eta V_m / Nh) \quad (6)$$

Where  $V_m$  is the average molar volume of solution, N is the Avogadro's number, and h= Plank's constant. The  $\Delta H_{\eta}^{\ddagger}$ ,  $\Delta G_{\eta}^{\ddagger}$  and  $\Delta S_{\eta}^{\ddagger}$  represents the change of enthalpy, free energy and entropy respectively during the process which are shown in Table 6. The  $\Delta G_{\eta}^{\ddagger}$  value is positive for all the studied systems. The positive free energy of activation for viscous flow can be interpreted with the help of Furth model [20] which states that the kinetic species involved in forming cavities or holes in the liquid medium is given by the work required in forming the hole against surface tension of the solution. It is seen that the  $\Delta G_{\eta}^{\ddagger}$  of DL-serine aqueous solutions increases very slowly with increase of solute concentration and decreases with the increase in temperature. The slow increase in property of  $\Delta G_{\eta}^{\ddagger}$  for aqueous amino acid solutions indicates that the structure destroying property is decreased with increase of solute concentration.

The variations of entropy of activation,  $\Delta S_{\eta}^{\ddagger}$ , for DL-serine in aqueous systems are noted in Tables 6. The  $\Delta S_{\eta}^{\ddagger}$  values for the flow process are positive in all cases but do not follow any specific pattern. This indicates that the water molecules at nonpolar–water interface do not have unique placement but adopt different arrangements depending on the surrounding atomic groups which may affect the entropy and enthalpy in different ways.

Tables 6 shows that the positive values of  $\Delta H_{\eta}^{\ddagger}$  indicate that positive work has to be done to overcome the energy barrier for the flow process.

**Table 6:** Activation parameters [free energy ( $\Delta G^{\ddagger}$ ), entropy ( $\Delta S^{\ddagger}$ ) and enthalpy ( $\Delta H^{\ddagger}$ )] in aqueous DL-serine solutions at T= (288.15, 295.15, 302.15, 309.15 and 316.15) K.

m /(mol.kg <sup>-1</sup> )	$\Delta G^{\ddagger}/\text{kJ mol}^{-1}$					$\Delta S^{\ddagger}$ /Jmol <sup>-1</sup> K <sup>-1</sup>	$\Delta H^{\ddagger}$ /KJ mol <sup>-1</sup> K <sup>-1</sup>
	288.15K	295.15K	302.15K	309.15K	316.15K		
0.0497	9.4749	9.2772	9.1068	8.9545	8.8180	23.2792	16.21895
0.1001	9.5037	9.3060	9.1493	8.9855	8.8695	22.7700	16.0418
0.1499	9.5273	9.3429	9.1922	9.0248	8.9205	21.9520	15.8334
0.2019	9.5506	9.3629	9.2225	9.0615	8.9554	21.3800	15.6897
0.2497	9.6027	9.3964	9.2452	9.0883	8.9846	22.1290	15.9488
0.2972	9.6307	9.4362	9.2893	9.1236	9.0141	22.1520	15.9912
0.3503	9.6484	9.4746	9.3219	9.1566	9.0409	21.9700	15.9657
0.4035	9.6834	9.5163	9.3700	9.1841	9.1025	21.4120	15.8399

#### IV. Conclusions

In summary, in the results of the above experiments, we confirmed that intermolecular interaction exist in the systems studies. The existence of ion–ion or solute–solute interaction resulting electrostrictive force enhance the structure breaking properties of DL-serine in aqueous system. The solute-solvent interaction, interstitial incorporation, hydrophilic hydration interaction renders the binary DL-serine systems more structured. This is reflectively the positive  $\Delta G_{\eta}^{\ddagger}$  value. Since the positive work has to be done to overcome the energy barrier for the flow process. That is, the viscous flow is not thermodynamically favored for the systems studied.

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