

**Volumetric and viscometric studies of  $\beta$ -alanine in water and ammonia solution at 293- 313K: structure making and breaking effect**

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Received January 2015; Accepted February 2015

**ABSTRACT**

The physicochemical properties of solute in solutions provide valuable information on solute – solvent, solute – solute and solvent – solvent interactions. The intermolecular forces between the liquids molecules and solvent molecules affect the viscosity of the solution. Information regarding inter and intra molecular interactions can be obtained from volumetric, and viscometric data in a solute solvent system. This study reports the volumetric and viscometric properties of solution of  $\beta$ -alanine at the concentration range of 0.05 - 0.5 mol dm<sup>-3</sup> in water and liquid ammonia at temperature range of 293 - 313K. Apparent molar volume at infinite dilution ( $\varphi_v^o$ ) was estimated from the least square fit of  $\varphi_v$  vs concentration. Viscosity coefficients A and B were calculated from the viscosity data Jones–Dole equation. Viscosity coefficients A and B were calculated from the viscosity data Jones–Dole equation. The activation parameters for viscous flow  $\Delta\mu_1^\ddagger$ ,  $\Delta\mu_2^\ddagger$ ,  $\Delta S_1^\ddagger$  and  $\Delta H_1^\ddagger$  were also estimated using Eyring equation. The data are explained vis-à-vis structure making or breaking effect of  $\beta$ -Alanine in the solvents under conditions of investigation.

**Keywords:**  $\beta$ -Alanine; Liquid ammonia; Apparent molar volume; Infinite dilution; Structure breaking and structure making

**INTRODUCTION**

The physicochemical properties of solute in solutions provide valuable information on solute – solvent, solute – solute and solvent – solvent interactions [1, 3]. The intermolecular forces between the liquids molecules and solvent molecules affect the viscosity of the solution. The effect on the viscosity and other parameters such as

temperature, nature and concentration of the solute had been exploited to obtain required information about the kind of interaction between the solutes and solvents molecule. This information is important in understanding the stability and several other biochemical and physiological processes that occur in living

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cell when the solute or solvent involved are biological molecules such as protein [4 – 9].

Studying protein may provide complex results which may be too cumbersome to interpret; therefore amino acids which are building blocks of proteins can be studied to understand the molecular interactions such as hydrogen bonding, ion-ion, ion-solvent solute-solvent etc. Investigation of volumetric and viscometric properties of amino acids in aqueous and mixed solvents can further be used to arrive at a handy result [10, 11].

Work place and other daily routines are some of the sources of getting contact with solvent or liquid such as ammonia. In the body system its high solubility in water makes it to be easily absorbed and this may affect the amino acid conformations, transportation and the products of their reactions. In this study we desired to study  $\beta$ -Alanine in water and liquid ammonia under different conditions to see whether it has no net effect on their structures either by enhancing or breaking their structure.

## MATERIAL AND METHOD

$\beta$ -alanine (98.5 %) and ammonia solution (25 %) were from BDH, London. Water for the solutions was doubly distilled. The densities were measured by using a 25 ml density bottle. The viscosities were measured by the Ubbelohde viscometer (Calibrated CUC (9721-K50) Series) from Cannon Instrument with sufficiently long efflux time to avoid kinetic energy correction. The time of flow was recorded by electronic digital clock capable of reading up to 0.01 s. A METTLER PM-200 electronic balance with accuracy of 0.0001 g was used for weighing. The temperature was controlled by a thermostatic water bath fluctuating to 0.1°C.

## RESULTS AND DISCUSSION

The values of densities ( $\rho$ ) and viscosities ( $\eta$ ), obtained for various concentrations of  $\beta$ -Alanine in water and ammonia at  $T = (293.15, 298.15, 303.15, 308.15, \text{ and } 313.15)$  K are listed in Tables 1 and 2. The apparent molar volumes, ( $\varphi_v$ ) were calculated from  $\rho$  data using the following relation.

$$\varphi_v = \frac{(M * C + 1000(\rho_0 - \rho))}{\rho_0 * C} \quad (1)$$

where  $\rho$  and  $\rho_0$  are the densities of solution and solvent (water or ammonia), respectively,  $C$  is the molar concentration of solute ( $\beta$ -Alanine) and  $M$  is its molar mass.

The apparent molar volume at infinite dilution ( $\varphi_v^o$ ) was obtained using a least-square fit to the linear plots of  $\varphi_v$  vs  $\sqrt{C}$  using the Masson equation [12]:

$$\varphi_v = \varphi_v^o + S_v \sqrt{C} \quad (2)$$

where  $S_v$  is the experimental slope, also known as the volumetric pairwise interaction coefficient [13, 14]. The values of limiting apparent molar volume ( $\varphi_v^o$ ) and  $S_v$  are also presented for  $\beta$ -Alanine in water and ammonia media as shown in Tables 1 and 2, the trends are also presented in Figures 1 – 2.

The negative values of  $S_v$  obtained for  $\beta$ -Alanine in the two solvents suggested weak solute – solute or ion - ion interactions.  $\varphi_v^o$  the intercept, is the limiting apparent molar volume of the solute, it provides information concerning solute – solvent interactions. The positive values of  $\varphi_v^o$  (Tables 1 and 2) suggest the presence of strong solute – solvent

interactions in these media throughout the  $\beta$ -Alanine concentrations and temperatures under investigations. The variation of  $\varphi_v^o$  with molar concentration of  $\beta$ -Alanine can be explained with co-sphere overlap model [15]. This model assumes that hydrophilic – ionic group interaction resulted in positive contribution to  $\varphi_v^o$  and that negative contribution is due to hydrophilic-hydrophobic interactions. The zwitterion forms of  $\beta$ -Alanine (i.e.  $-\text{NH}_3^+$ ,  $\text{COO}^-$ ) as well as the side chain of the amino acid play significant role in interaction with solvent ion hence a positive value of  $\Delta\varphi_v^o$  [7, 16]. Tables 1 and 2 also revealed increasing density of the solutions with  $\beta$ -Alanine concentrations, this is also a confirmation of attraction between the solute and solvent molecules.

The temperature dependence of  $\varphi_v^o$  was according to the relation;

$$\varphi_v^o = a_1 + a_2T + a_3T^2 \quad (3)$$

Values of coefficients  $a_i$  and the limiting apparent molar expansivity  $\frac{\partial\varphi_v^o}{\partial T}$  obtained by least.

The values of the limiting apparent molar expansivity is decreasing with in increasing temperature at the concentration of 0.05 and 0.2 mol  $\text{dm}^{-3}$  in ammonia this is a clear indication of common salt behaviour in this concentration region. However in water the increase in temperature lead to sharp increase in the molar expansivity this is attributed to complete solute – solvent co-sphere behaviour of alanine in water. The values thermal expansivities  $\frac{\partial^2\varphi_v^o}{\partial T^2}$  estimated (Table

4) showed that  $\beta$ -alanine is a structure breaker in water whereas it is a structure maker in ammonia [17].

The viscosity was determined from the relative viscosity using the relation:

$$\frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \quad (4)$$

where  $\eta$ ,  $t$  and  $\rho$  are the absolute viscosity, time of flow and density of solution, while  $\eta_0$ ,  $t_0$  and  $\rho_0$  are same quantities for the solvent (water or ammonia).

The viscosity data was analysed by least square fit of relative viscosity vs concentration variation according to Jones-Dole equation below:

$$\frac{\eta}{\eta_0} = \eta_r = 1 + A^*C^{1/2} + BC \quad (5)$$

where  $\eta_r$  is relative viscosity,  $C$  is molar concentration the constant  $A$  is the Falkenhagen coefficient and  $B$  is the Jones-Dole coefficient related to solute-solvent and solute-solute interaction respectively. The value of viscosity coefficient  $A$  is also associated with the size of the solutes, the coefficients  $A$  and  $B$  of the Jones–Dole equation have been determined and the results is presented in Table 5.

The thermodynamic properties were estimated using the Nightingale and Benck and Eyring equations [18]. The average Gibbs energy of activation of a solute for viscous flow in a solvent can be calculated from the viscosity by the relation:

$$\eta_0 = \frac{hN_A}{V_1^0} \exp[\Delta\mu_1^\ddagger RT] \quad (6)$$

where  $h$  and  $N_A$  are the Planck's constant and Avogadro's number, respectively, and  $V_1^0$  is the average molar volume which is practically equal to  $\varphi_v^o$ . The activation Gibbs energy,  $\Delta\mu_1^\ddagger$  for viscous flow of the L-Alanine in water and ammonia is related to the coefficient  $B$  of viscosity by:

$$B = \left[ \frac{(\bar{V}_1^0 - \bar{V}_2^0)}{1000} \right] + \bar{V}_2^0 \left[ \frac{(\Delta\mu_2^\ddagger - \Delta\mu_1^\ddagger)}{1000RT} \right] \quad (7)$$

Upon rearrangement the expression in Eq. (7) above becomes:

$$\Delta\mu_2^\# = \Delta\mu_1^\# + \left(\frac{RT}{\bar{V}_1^0}\right) \left[1000B - (\bar{V}_1^0 - \bar{V}_2^0)\right] \quad (8)$$

where R is gas constant and T is the absolute temperature respectively.

The calculated values of  $\Delta\mu_1^\#$  and  $\Delta\mu_2^\#$  values are negative for all the studied systems as displayed in Table 5. This is interpreted on the basis of solute – solvent interaction leading to the formation of more structured systems.

Figures 5 and 6 also depict the change in viscosity with increase concentration of  $\beta$ - alanine in water and ammonia respectively. From this figures increasing in molar volume also affect the viscosity differently in the two solvents. It is observed that the values of A are positive only in ammonia while the values of B are all positive in water. This is a clear

indication of presence of strong ionic interactions between the  $\beta$ -Alanine molecules with existence of weak existence of ion – solvent interactions. The reverse is observed in water – alanine system.

Other activation parameters reported in Table 5 i.e.  $\Delta H_1^\#$  and  $\Delta S_1^\#$  were obtained from the relations:

$$\Delta\mu_1^\# = \Delta H_1^\# - T\Delta S \quad (9)$$

Considering the activation parameters, the systems appeared to be more structured in ammonia than in awater as indicated by higher values  $\Delta S_1^\#$  in water than in ammonia. The values of  $\Delta H_1^\#$  suggested that less work is required to dissolve  $\beta$ -alanine in ammonia than in water.

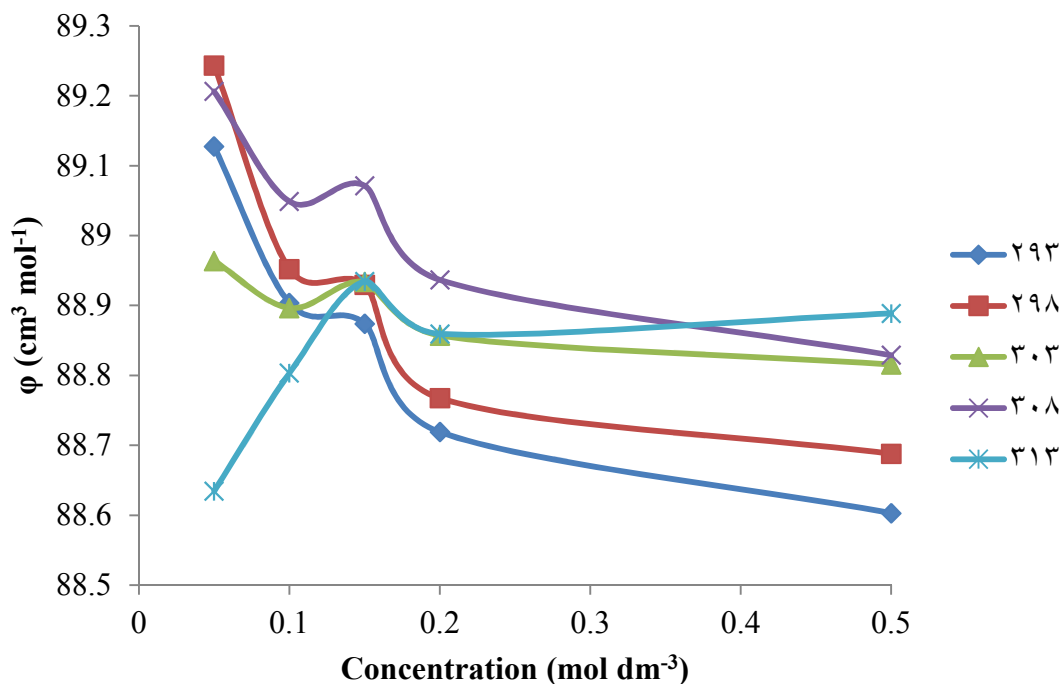


Fig. 1. Partial molar volume vs concentration for water +  $\beta$ -Alanine system.

**Table 1.** The density ( $\rho$ ), viscosity ( $\eta$ ), partial molar volume ( $\varphi_v$ ) apparent molar volume ( $\varphi_v^o$ ) and pairwise coefficient ( $S_v$ ) of L-Alanine in Liquid Ammonia at various concentration and temperature

Temp (K)	Conc (mol dm <sup>-3</sup> )	$\rho$ (g cm <sup>-3</sup> )	$\eta$ (Ns m <sup>-2</sup> )	$\varphi_v$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\varphi_v^o$ (cm <sup>3</sup> mol <sup>-1</sup> )	$S_v$ (cm <sup>3</sup> dm <sup>3/2</sup> mol <sup>-1</sup> )
	0.000	0.6103			100.3632	-9.5415
293 K	0.050	0.6197	1.0242	99.8660	98.2297	
	0.100	0.6292	1.0288	96.6576	97.3459	
	0.150	0.6387	1.0046	95.7230	96.6678	
	0.200	0.6483	1.0288	95.2497	96.0961	
	0.500	0.7342	1.0273	94.4595	93.6163	
298 K	0.000	0.6029			106.5523	-18.1235
	0.050	0.6123	1.0242	106.0547	102.4997	
	0.100	0.6217	1.0274	98.3665	100.8211	
	0.150	0.6313	1.0097	98.4993	99.5331	
	0.200	0.6409	1.0193	96.7975	98.4472	
	0.500	0.7268	1.0821	95.3202	93.7370	
303 K	0.000	0.5952			97.76467	-3.70786
	0.050	0.6048	1.0083	97.7436	96.9356	
	0.100	0.6143	1.0233	96.1630	96.5921	
	0.150	0.6239	1.0433	95.9337	96.3286	
	0.200	0.6334	1.0566	95.7346	96.1065	
	0.500	0.7191	1.0815	95.5307	95.1428	
308 K	0.000	0.5882			96.88905	-1.26029
	0.050	0.5977	1.0092	97.0173	96.6072	
	0.100	0.6073	1.0351	96.0223	96.4905	
	0.150	0.6168	1.0425	96.5158	96.4009	
	0.200	0.6264	1.0444	96.1254	96.3254	
	0.500	0.7121	1.146	96.1412	95.9979	
313 K	0.000	0.5795			97.33391	-1.95059
	0.050	0.5891	1.0686	97.3029	96.8977	
	0.100	0.5987	1.0571	96.2945	96.7171	
	0.150	0.6083	1.0514	96.8008	96.5785	
	0.200	0.6179	1.0343	96.0698	96.4616	
	0.500	0.7034	1.0552	96.1415	95.9546	

**Table 2.** The density ( $\rho$ ), viscosity ( $\eta$ ), partial molar volume ( $\varphi_v$ ) apparent molar volume ( $\varphi_v^o$ ), pairwise coefficient ( $S_v$ ) and transfer volume,  $\Delta\varphi_v^o$  of L-Alanine in water at various concentrations and temperature

Temp (K)	Conc (mol. dm <sup>-3</sup> )	$\rho$ (g cm <sup>-3</sup> )	$\eta$ (Ns m <sup>-2</sup> )	$\varphi_v$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\varphi_v^o$ (cm <sup>3</sup> mol <sup>-1</sup> )	$S_v$ (cm <sup>3</sup> dm <sup>1/2</sup> mol <sup>-3/2</sup> )	$\Delta\varphi_v^o$ (cm <sup>3</sup> mol <sup>-1</sup> )
	0	0.998234			89.26787	-1.01466	11.09533
293 K	0.05	1.006187	1.0019	89.1277	89.04099		9.188665
	0.1	1.014142	1.0093	88.9038	88.94701		8.3989
	0.15	1.02212	1.0186	88.8739	88.8749		7.792893
	0.2	1.030105	1.0538	88.719	88.8141		7.282005
	0.5	1.122134	1.0835	88.603	88.5504		5.065936
298 K	0	1.017389			89.34685	-1.03437	17.20542
	0.05	1.025254	1.0039	89.24365	89.11556		13.38418
	0.1	1.033121	1.0232	88.95234	89.01976		11.80137
	0.15	1.041012	1.0502	88.92993	88.94625		10.58684
	0.2	1.048903	1.0656	88.76746	88.88427		9.562937
	0.5	1.141289	1.11	88.68791	88.61545		5.121593
303 K	0	0.995678			89.01431	-0.29063	8.750357
	0.05	1.003642	0.9569	88.96378	88.94933		7.98624
	0.1	1.011603	0.9745	88.8964	88.92241		7.669732
	0.15	1.019577	0.9882	88.93383	88.90175		7.426868
	0.2	1.027552	0.9941	88.85709	88.88434		7.222123
	0.5	1.119578	0.998	88.81553	88.80881		6.334007
308 K	0	0.994152			89.32544	-0.73747	7.563608
	0.05	1.002116	0.9259	89.20626	89.16054		7.446703
	0.1	1.010077	0.9506	89.04899	89.09223		7.398279
	0.15	1.01806	0.9733	89.07146	89.03982		7.361122
	0.2	1.02605	0.9959	88.93666	88.99563		7.329797
	0.5	1.118052	1.0309	88.82881	88.80397		7.19392
313 K	0	0.992247			88.65167	0.414077	8.682246
	0.05	1.000231	0.8694	88.63455	88.74426		8.15349
	0.1	1.008203	0.8758	88.80321	88.78261		7.934472
	0.15	1.016191	0.92	88.93438	88.81204		7.766413
	0.2	1.024167	0.9663	88.85942	88.83685		7.624734
	0.5	1.116147	0.9895	88.88866	88.94446		7.010172

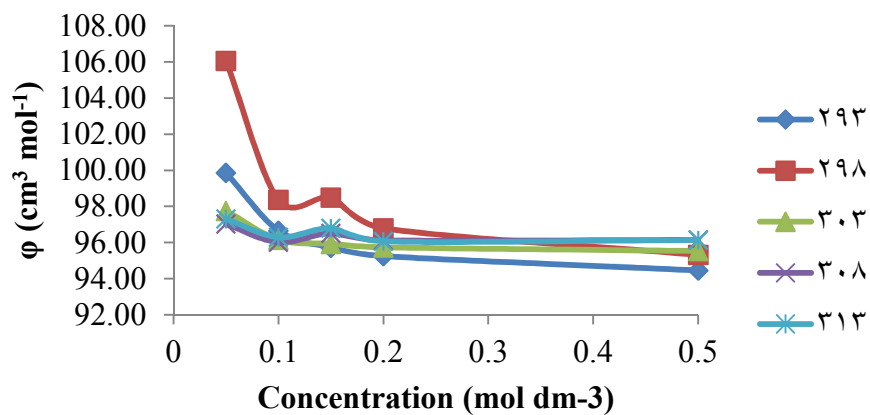


Fig. 2. Partial molar volume vs concentration for Ammonia +  $\beta$ - Alanine system.

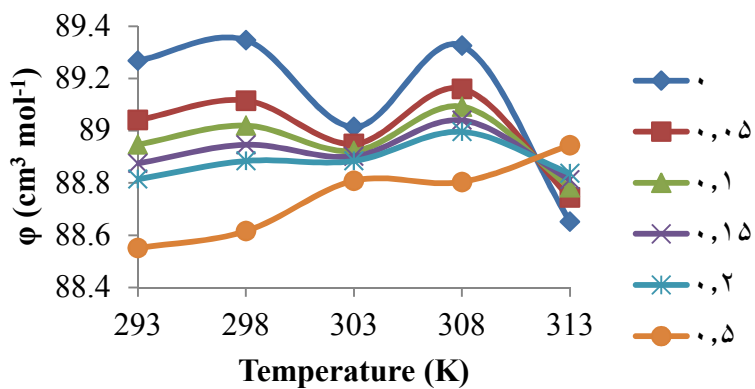


Fig. 3. Change in molar volume with increase Temperature of  $\beta$ - alanine in water.

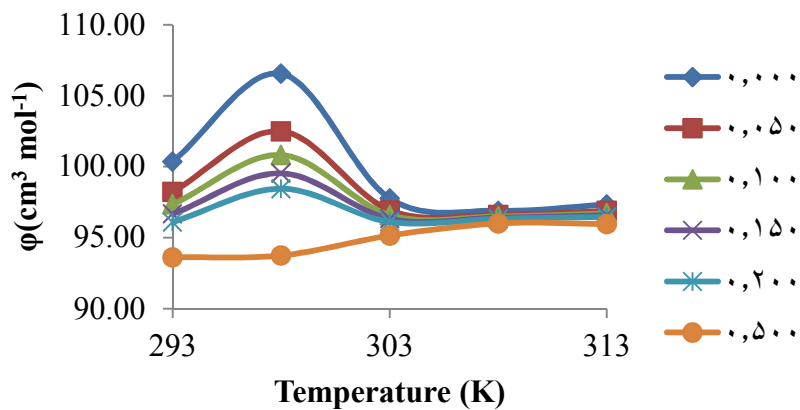


Fig. 4. Change in molar with increase Temperature of  $\beta$ - alanine in ammonia.

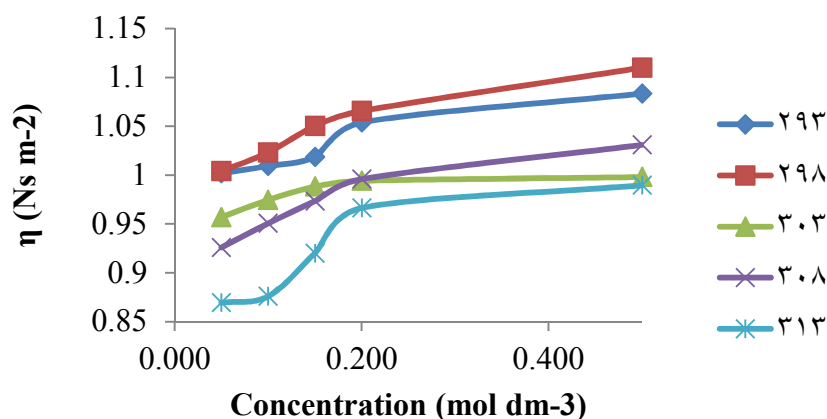


Fig. 5. Change in viscosity with increase concentration of  $\beta$ - alanine in water.

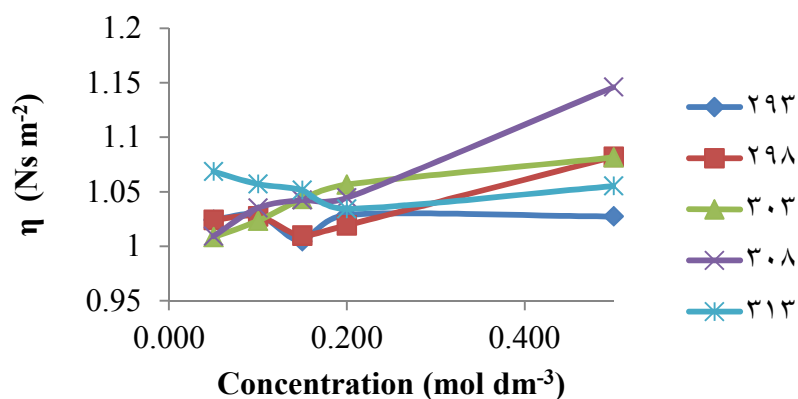


Fig. 6. Change in viscosity with increase concentration of  $\beta$ - alanine in ammonia.

Table 3. Values of coefficients  $a_i$  for L-Alanine in water and Liquid Ammonia

Conc (mol dm <sup>-3</sup> )	Coefficient of expansion (Liquid Ammonia)			Coefficient of expansion (Water)		
	$a_1$ (cm <sup>3</sup> mol <sup>-1</sup> )	$a_2$ (cm <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )	$a_3$ (cm <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )	$a_1$ (cm <sup>3</sup> mol <sup>-1</sup> )	$a_2$ (cm <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )	$a_3$ (cm <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )
0	1270.265	-7.583	0.012	-363.6710	3.0161	-0.0050
0.05	745.287	-4.211	0.007	-207.8876	1.9721	-0.0033
0.1	527.8437	-2.8145	0.0046	-143.3600	1.5396	-0.0025
0.15	360.9876	-1.7427	0.0029	-93.8463	1.2078	-0.0020
0.2	220.2669	-0.8388	0.0014	27.8080	0.4024	-0.0007
0.5	-177.500	1.660	-0.003	70.4268	0.1014	-0.0001



**Table 4.** Values of coefficients Limiting apparent molar and thermal expansivity for L-Alanine in water and Liquid Ammonia

Temp (K)	293	298	303	308	313	$\frac{\partial^2 \phi_v^0}{\partial T^2}$	Limiting apparent molar expansibility in Liquid Ammonia $\frac{\partial \phi_v^0}{\partial T}$					$\frac{\partial^2 \phi_v^0}{\partial T^2}$
	293	298	303	308	313		293	298	303	308	313	
Conc (mol dm <sup>-3</sup> )	Limiting apparent molar expansibility in Liquid Ammonia $\frac{\partial \phi_v^0}{\partial T}$											
	293	298	303	308	313	0.024509	0.0753	0.0251	-0.0251	-0.0753	-0.1254	-0.01004
0.0000	-0.4022	-0.2797	-0.1571	-0.0346	0.0880	0.013671	0.0545	0.0218	-0.0110	-0.0437	-0.0764	-0.00654
0.0500	-0.2055	-0.1372	-0.0688	-0.0005	0.0679	0.009182	0.0459	0.0204	-0.0051	-0.0306	-0.0561	-0.0051
0.1000	-0.1241	-0.0781	-0.0322	0.0137	0.0596	0.005738	0.0392	0.0193	-0.0006	-0.0206	-0.0405	-0.00399
0.1500	-0.0615	-0.0329	-0.0042	0.0245	0.0532	0.002833	0.0141	0.0075	0.0008	-0.0058	-0.0124	-0.00133
0.2	-0.00882	0.005339	0.019502	0.033666	0.047829	-0.00502	0.0222	0.0209	0.0195	0.0182	0.0168	-0.00027

**Table 5.** Viscosity coefficients and Activation for viscosity of L-Alanine in Water and Liquid Ammonia

	Liquid Ammonia+ L – Alanine (Temperature K)					Water + L – Alanine (Temperature K)				
	293	298	303	308	313	293	298	303	308	313
A (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	0.089	0.004	0.071	-0.018	0.243	-0.00655	0.044098	-0.13187	-0.28769	-0.55798
B (dm <sup>3</sup> mol <sup>-1</sup> )	-0.07472	0.148958	0.070619	0.314143	-0.24839	0.184267	0.166709	0.19406	0.487543	0.801673
$\Delta \rho_1^\ddagger$ (kJ mol <sup>-1</sup> )	-0.05761	-0.05661	-0.05571	-0.0548	-0.05393	-0.05765	-0.05668	-0.05577	-0.05487	-0.05401
$\Delta \rho_2^\ddagger$ (kJ mol <sup>-1</sup> )	-0.05942	-0.05315	-0.05389	-0.0465	-0.04057	-0.05262	-0.05206	-0.05028	-0.04089	-0.03048
$\Delta H_1^\ddagger$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	0.0010	0.0030	0.0049	0.0068	0.0087	0.5283	0.5393	0.5502	0.5611	0.5720
$\Delta S_1^\ddagger$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	0.0002	0.0002	0.0002	0.0002	0.0002	0.0020	0.0020	0.0020	0.0020	0.0020

## CONCLUSION

The density and viscosity of  $\beta$ -Alanine in aqueous and ammonia as a function of concentration at the temperature ranges between 293 and 313 K had been studied. The results showed that:

- i. partial molar volume ( $\phi_v$ ) and apparent molar volume at infinite dilution ( $\phi_v^o$ ) are concentration and temperature dependent in both water and ammonia.
- ii. solute – solvent interaction predominate the solution of  $\beta$ -Alanine in water and ammonia, however, solute – solute interaction is more pronounced in ammonia.
- iii. The activation parameters for viscous flow  $\beta$ -Alanine solution in the two solvent present an ordered structure in ammonia than in water.

In water,  $\beta$ -Alanine behave as a structure breaker and whereas in ammonia it is a structure maker. Considering the activation parameters, the systems appeared to be more structured.

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