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Viscometric, Volumetric and Thermodynamic Studies L-Alanine in Aqueous and Ethanol Media at 293 – 313 K

Abideen Idowu Adeogun*[1, 2] Mopelola Abidemi Idowu[1], Sikiru Akinyeye Ahmed[3], Niniola Mariam Oyedokun[1]
[1]Chemistry Department Federal University of Agriculture, Abeokuta, Nigeria
[2]Pollution Control Division, Central Electrochemical Research Institute, Karaikudi, 630006, Tamil Nadu, India
[3]Chemistry Department Ondo State University of Science and Technology, Okitipupa, Nigeria

ABSTRACT

Valuable information regarding solute – solvent, solute – solute and solvent – solvent interactions are obtainable from volumetric, viscometric and other thermodynamic data in a solute solvent system. Consequently we study the density and viscosity of L-Alanine in aqueous and ethanol media as a function of concentration at the temperature ranges between 293 and 313 K. The apparent molar volume (φ_υ) of the amino acid is linearly related to its concentration in the two media. Apparent molar volume at infinite dilution (φ_v^o) were estimated from least square fit of φ_v vs molarity. Viscosity coefficients A and B were calculated from the viscosity data Jones–Dole equation. The activation parameters for viscous flow $\Delta\mu_1^{\#}, \Delta\mu_2^{\#}, \Delta S_1^{\#}$ and $\Delta H_1^{\#}$ were also estimated using Eyring equation. The data are explained vis-à-vis structure making or breaking effect of L-Alanine at the temperature under consideration.

Key words: L-Alanine; ethanol; apparent molar volume; infinite dilution; structure breaking and structure making

I. INTRODUCTION

The physicochemical properties of solutes in solutions provide valuable information on solute – solvent, solute – solute and solvent – solvent interactions. When applied to proteins, information that are important in understanding their stability and several other biochemical and physiological processes in a living cell are obtainable (Pal *et al.*, 2009; Zhao, 2006; Zhuo *et al.*, 2005; Banipal *et al.*, 2009; Nain, 2013; Thirumaran and Imban, 2011).

Proteins are large complex molecules with high difficulty in direct study of their interactions with solvents. Therefore, one useful approach is to investigate interactions of the model compounds of proteins, i.e. amino acids, in aqueous or mixed solvent system. The extensive studies of volumetric properties of amino acids in various solvent media can act as effective probes of their confirmation and properties in solutions (Wadi *et al.*, 1992; Banipal *et al.,* 2004; Yan *et al.,* 2001).

L-Alanine, a nonessential α-amino acid is manufactured by the human body and does not need to be obtained directly through the diet. It is manufactured in the liver from other amino acids. It is one of the most widely used amino acids in the "fabrication" of proteins, reinforcing their flexibility, fibre-strength and resilience. It is readily converted to glucose when blood sugar levels fall. Life style, work place and dietary are major sources of getting alcohol absorbs into the body system, with effects depending on amount absorbed. When mixed with body fluids can affect the conformation, transportation and the products of their reactions. In this study we desired to study L-Alanine in aqueous and ethanol system under different conditions to see whether it has no net effect on water and ethanol structures either by enhancing or breaking their structure.

II. METHODS AND MATERIAL

L-alanine (98.5 %) and Ethanol (99.8 %) were from BDH, London. L-Alanine was recrystallized in water + ethanol and dried in desiccator for 24 hours prior to use. Water for the solutions was doubly distilled. The densities were measured by using a 25 ± 0.01 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 ^{o}C.

III. RESULTS AND DISCUSSION

The values of densities (ρ) and viscosities (η), obtained for various concentrations of L-Alanine in water and ethanol at $T = (293.15, 298.15, 303.15, 308.15,$ and $313.15)$ K are listed in Tables 1 and 2. The apparent molar volumes, (φ_v) were calculated from ρ data using the following relation:

$$\varphi_\upsilon = M/\rho - 1000(\rho_0 - \rho)/\rho_0\rho m \tag{1}$$

where ρ and ρ_0 are the densities of solution and solvent (water or ethanol), respectively, m is the concentration of the solute (L-Alanine) in molality and M is its molar mass of the solute.

The apparent molar volume at infinite dilution (φ_v^o) was obtained using a least-square fit to the linear plots of φ_v vs m using the Masson equation (Masson, 1929):

$$\varphi_v = \varphi_v^o + S_v\sqrt{m} \tag{2}$$

where S_v is the experimental slope, also known as the volumetric pairwise interaction coefficient (Desnoyers, 1982; Hedwig, 1991). The values of the limiting apparent molar volume, φ_v^o and the volumetric pairwise interaction coefficient, S_v are also presented for L-Alanine in ethanol and water are as shown in Tables 1 and 2. There are slight variations in the values of φ_v and φ_v^o as the temperature varies. The positive values of φ_v^o (Tables 1 and 2) suggest the presence of strong solute – solvent interactions in these media throughout the L-Alanine concentrations and temperatures under investigations. The variation of φ_v^o with molar concentration of L-Alanine can be explained with co-sphere overlap model (Gurney 1953). This model assumes that hydrophilic – ionic group interaction resulted in positive contribution to φ_v^o and that negative contribution is due to hydrophilic-hydrophobic interactions. The zwitterionic forms of amino acids (i.e. -NH_3^+, COO^-) as well as their side chains play significant roles in their interaction with solvents ion hence a positive value of $\Delta\varphi_v^o$ (Banipal *et al.*, 2009, Nain 2009). The trends are also presented in Figures 1 and 2.

Table 1: The density (ρ), viscosity (η), partial molar volume (φ_v) apparent molar volume (φ_v^o) and pairwise coefficient (S_v) of L-Alanine in Water at various concentration and temperature.

Temp /K	molality. /(mol kg^{-1})	ρ /(g cm^{-3})	η /(Ns m^{-2})	φ_v /(cm^3 mol^{-1})	φ_v^o /(cm^3 mol^{-1})	S_v /(cm^3 dm$^{3/2}$ mol^{-1})
293	0.000	0.998			61.104	-2.786
	0.050	1.000	1.0148	60.341	60.483	
	0.099	1.001	1.0500	60.226	60.227	
	0.148	1.002	1.0500	60.141	60.031	
	0.197	1.004	1.0407	59.999	59.867	
	0.484	1.012	1.0611	59.068	59.166	
298	0.000	0.997			60.342	-1.155
	0.050	0.999	1.0585	59.772	60.085	
	0.099	1.000	1.0245	60.179	59.978	
	0.148	1.001	1.0094	60.053	59.897	
	0.197	1.003	1.0981	59.919	59.829	
	0.483	1.011	1.1226	59.405	59.539	
303	0.000	0.996			61.000	-2.727
	0.050	0.997	1.1104	60.279	60.392	
	0.099	0.999	1.1083	60.166	60.142	
	0.148	1.000	1.0833	60.028	59.951	
	0.197	1.001	1.0729	59.866	59.790	
	0.483	1.010	1.1646	59.036	59.105	
308	0.000	0.999			61.096	-2.510
	0.050	1.001	1.0224	60.468	60.535	
	0.099	1.002	1.0306	60.305	60.305	
	0.149	1.004	1.0306	60.165	60.128	
	0.197	1.005	1.0469	60.064	59.980	
	0.484	1.013	1.0755	59.299	59.348	
313	0.000	0.992			60.951	-2.652
	0.049	0.994	1.0319	60.260	60.362	
	0.099	0.995	1.0298	60.161	60.119	
	0.147	0.996	1.0277	59.944	59.933	
	0.196	0.998	1.0213	59.877	59.777	
	0.481	1.006	1.0787	59.046	59.113	

Table 2: The density (ρ), viscosity (η), partial molar volume (φ_v)apparent molar volume (φ_v^o), pairwise coefficient (S_v) and transfer volume, $\Delta\varphi_v^o$ of L-Alanine in ethanol at various concentrations and temperature.

Temp /K	molality /(mol kg^{-1})	ρ /(g cm^{-3})	η /(Ns m^{-2})	φ_v /(cm^3 mol^{-1})	φ_v^o /(cm^3 mol^{-1})	S_v /(cm^3 dm$^{3/2}$ mol^{-1})
293	0.000	0.785			59.324	-1.700
	0.039	0.787	1.225	58.681	58.988	
	0.078	0.788	1.203	59.167	58.850	
	0.116	0.789	1.165	58.751	58.744	
	0.155	0.790	1.143	58.746	58.656	
	0.377	0.798	1.176	58.173	58.281	
298	0.000	0.781			60.238	-3.882
	0.039	0.782	1.140	59.265	59.472	
	0.077	0.784	1.061	59.285	59.157	
	0.116	0.785	1.073	59.012	58.917	
	0.154	0.786	1.044	58.780	58.716	
	0.375	0.794	1.044	57.762	57.862	
303	0.000	0.777			60.307	-3.849
	0.039	0.778	1.091	59.404	59.550	
	0.077	0.779	1.008	59.331	59.239	
	0.115	0.781	1.063	58.947	59.001	
	0.153	0.782	1.077	58.973	58.803	
	0.372	0.789	1.056	57.856	57.958	
308	0.000	0.790			50.453	-5.062
	0.039	0.791	1.064	49.292	49.449	
	0.078	0.793	1.036	49.168	49.036	
	0.117	0.794	1.035	48.846	48.721	
	0.156	0.796	1.051	48.426	48.457	
	0.380	0.805	1.035	47.296	47.332	
313	0.000	0.772			48.404	-5.432
	0.038	0.774	1.353	47.157	46.900	
	0.077	0.776	1.073	47.024	46.565	
	0.115	0.777	1.066	46.679	46.285	
	0.152	0.779	1.056	46.229	45.092	
	0.372	0.788	1.062	45.015	48.404	

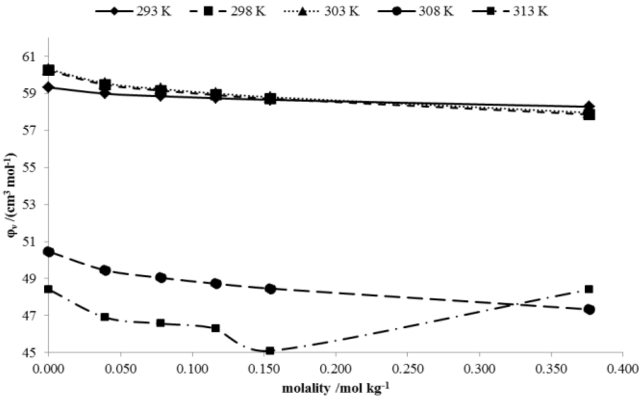

Figure 1: Partial molar volume vs concentration for Ethanol- Alanine system.

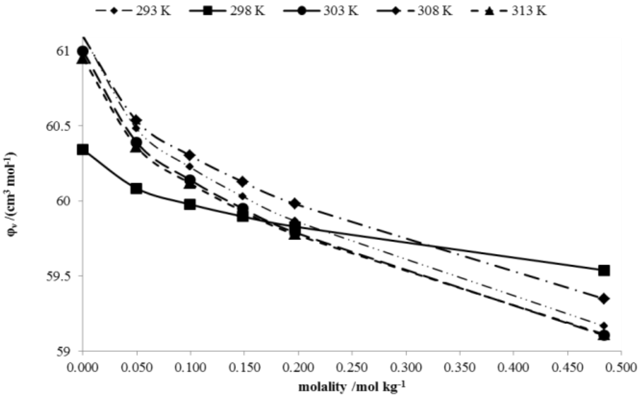

Figure 2: Partial molar volume vs concentration for Water - Alanine system

The negative values of S_v obtained for L-Alanine in the two solvents suggested weak solute – solute or ion ion interactions. φ_v^o , the intercept, which is the limiting apparent molar volume of the solute, provides information concerning solute – solvent interactions. Tables 1 and 2 also revealed increasing density of L-Alanine with increasing concentrations; this is also a confirmation of attraction between the solute and solvent molecules. The temperature dependence of φ_v^o was according to the relation in equation 3 below:

$$\varphi_v^0 = a_1 + a_2 T + a_3 T^2 \tag{3}$$

Figures 3 and 4 also depict the variations in the limiting apparent molar volume with temperature.

Table 3: Values of coefficients *ai* for L-Alanine in water and ethanol

Conc (mol dm^{-3})	Coefficient of expansion Alanine – Ethanol system			Coefficient of expansion (Alanine – water system)		
	a_1 (cm^3 mol^{-1})	a_2 / (cm^3 mol^{-1} K^{-1})	a_3/ (cm^3 mol^{-1} K^{-2})	a_1/ (cm^3 mol^{-1})	a_2 / (cm^3 mol^{-1} K^{-1})	a_3/ (cm^3 mol^{-1} K^{-2})
0.05	162.90	-0.69	0.0012	-3858.30	26.50	-0.04
0.10	49.22	0.07	-0.0001	-3599.25	24.82	-0.04
0.15	34.51	0.17	-0.0003	-3641.85	25.10	-0.04
0.20	70.25	-0.07	0.0001	-3716.80	25.61	-0.04
0.50	-83.59	0.95	-0.0016	-3497.54	24.19	-0.04

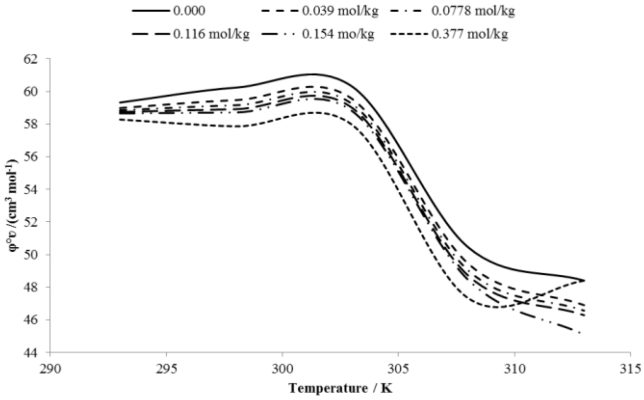

Figure 3: Change in limiting apparent molar volume with temperature in ethanol - L- alanine system.

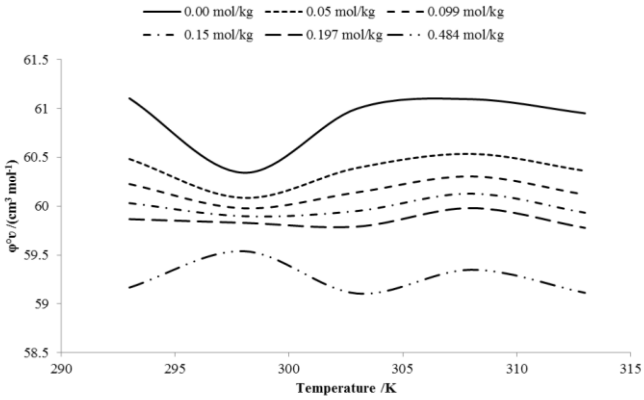

Figure 4: Change in limiting apparent molar volume with temperature in water - L- alanine system.

Values of coefficients a_i and the limiting apparent molar expansivity $\frac{\partial \varphi_v^0}{\partial T}$ obtained by least square fit are presented in Table 3 and 4. The values limiting apparent molar expansivity decreases with increasing temperature in ethanol which is a clear indication of common salt behaviour, and that at high temperature bonded solvent molecules are less hence expansivity become weaker (Huiyong et al., 2012). The increase in temperature lead to increase in the molar expansivity at 0.05 and 0.2 mol dm^3 this is attributed to complete solute-solvent co-sphere behaviour of alanine in water at these concentrations. The values thermal expansivities $\frac{\partial^2 \varphi_v^0}{\partial T^2}$ estimated (Table 4) showed that L-Alanine is a structure maker in both solvents with more effect in water than in ethanol at high concentration (Gupta and Sigh, 2005).

Table 4: Values of coefficients Limiting apparent molar and thermal expansivity for L-Alanine in water and ethanol

Temp /K	293	298	303	308	313	$\frac{\partial^2 \varphi_v^0}{\partial T^2}$	293	298	303	308	313	$\frac{\partial^2 \varphi_v^0}{\partial T^2}$
Conc/ (mol dm^{-3})	Limiting apparent molar expansibility in water $\frac{\partial \varphi_v^0}{\partial T}$						Limiting apparent molar expansibility (Ethanol) $\frac{\partial \varphi_v^0}{\partial T}$					
0.05	-0.0124	-0.0009	0.0107	0.0222	0.0338	0.0023	0.2361	-0.2122	-0.6604	-1.1087	-1.5569	-0.0897
0.10	0.0023	0.0011	-0.0001	-0.0013	-0.0025	-0.0002	0.1538	-0.2671	-0.6881	-1.1090	-1.5299	-0.0842
0.15	0.0003	-0.0027	-0.0056	-0.0086	-0.0116	-0.0006	0.1648	-0.2607	-0.6862	-1.1117	-1.5372	-0.0851
0.20	-0.0041	-0.0030	-0.0020	-0.0009	0.0001	0.0002	0.1609	-0.2734	-0.7078	-1.1421	-1.5764	-0.0869
0.50	0.0283	0.0127	-0.0030	-0.0187	-0.0343	-0.0031	0.0869	-0.3244	-0.7356	-1.1469	-1.5582	-0.0823

Table 5: Viscosity coefficients and Activation for viscosity of L-Alanine in Water and Ethanol

	Water + L – Alanine					Ethanol + L – Alanine				
(Temperature /K)	293	298	303	308	313	293	298	303	308	313
A /(dm$^{3/2}$ mol$^{-1/2}$)	0.135	0.669	1.568	2.139	2.496	0.077	0.038	0.348	0.798	1.931
B /(dm^3 mol^{-1})	-0.073	-0.433	-1.359	-1.963	-2.296	-0.121	-0.146	-0.347	-0.830	-2.257
$\Delta\mu_1^{\#}$ /(kJ mol^{-1})	62.208	62.208	62.208	62.208	62.208	62.490	62.490	62.490	62.490	62.490
$\Delta\mu_2^{\#}$ /(kJ mol^{-1})	56.92	42.01	3.64	-22.55	-38.38	55.26	54.19	45.64	18.00	-61.25
T $\Delta S_2^{\#}$ /(kJ mol^{-1})	-1495.18	-1520.69	-1546.21	-1571.724	-1597.24	-1577.51	-1604.43	-1631.35	-1658.272	-1685.19
$\Delta H_2^{\#}$ /(kJ mol^{-1}K^{-1})	-1438.26	-1478.68	-1542.57	-1594.27	-1635.61	-1522.25	-1550.25	-1585.71	-1640.27	-1746.44

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

$$\eta/\eta_0 = t\rho/t_0\rho_0 \qquad (4)$$

where η, t and ρ are the absolute viscosity, time of flow and density of solution, while η_0 , t_0 and ρ_0 are same quantities for the solvent (water or ethanol).

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

$$\eta/\eta_0 = \eta_r = 1 + A * C^{1/2} + B * C \qquad (5)$$

where η_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 co-efficient A is associated with the size of the soluteues of coefficients *A* and *B* of the Jones–Dole equation have been determined and the results is presented in Table 5 along with thermodynamic parameters of dissolution of L-Alanine in water and alcohol. Figures 5 and 6 also depict the change in viscosity with increase concentration of L- alanine in water and ethanol respectively. It is observed that the values of *A* are positive, while the values of B are negative in both solvent. This is a clear indication of presence of strong ionic interactions between the L-alanine molecules but weak ion – solvent interactions.

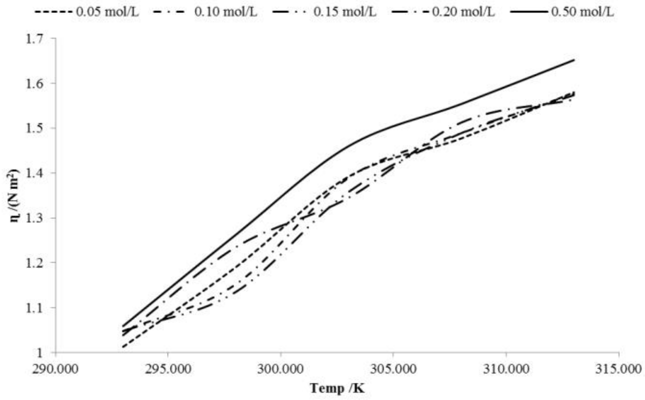

Figure 5 : Change in viscosities with temperature in ethanol- L- alanine system.

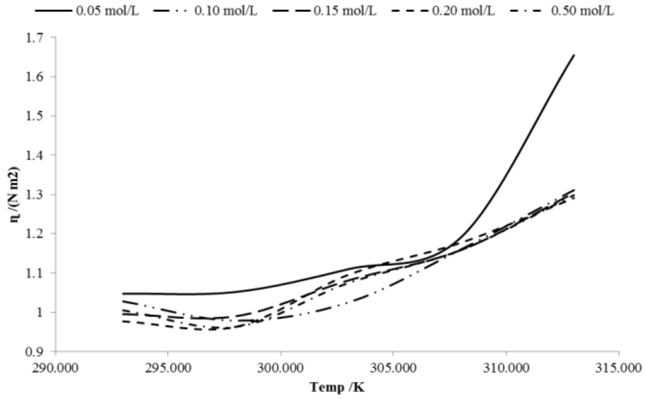

Figure 6: Change in viscosities with temperature in water- L- alanine system.

The thermodynamic properties were estimated using the Nightingale and Benck and Eyring equations (Hossain *et al.*, 2010). The average Gibbs energy of activation, $\Delta\mu_1^\#$ of a solute for viscous flow in a solvent can be calculated from the viscosity by the relation:

$$\Delta\mu_1^\# = RT\ln\left(\bar{V}_1^0\eta_0 / hN_A\right) \qquad (6)$$

IV. CONCLUSION

The density and viscosity of L-Alanine in water and ethanol as a function of concentration at the temperature ranges between 293 and 313 K have been studied. The results were used for the estimations of partial molar volume (φ_υ), apparent molar volume at infinite dilution (φ_v^o), and viscosity coefficients A and B. The activation parameters for viscous flow $\Delta\mu_1^\#, \Delta\mu_2^\#, \Delta S_1^\#$ and $\Delta H_1^\#$ were also estimated using Eyring equation. The data were explained vis-à-vis structure making or breaking effect of L-Alanine at the temperature under consideration. This study shows that there greater solute

where η_0, h and N_A are the solvent viscosity, Planck's constant and Avogadro's number, respectively, and $\bar{V}_1^0$ is the average molar volume which is practically equal to φ_v^o. The activation Gibbs energy, $\Delta\mu_1^\#$ for viscous flow of the L-Alanine in water and ethanol is related to the coefficient B of viscosity by:

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

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

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

where $\bar{V}_2^0$ is the molar volume of the solute, R is gas constant and T is the absolute temperature respectively. The calculated values of $\Delta\mu_1^\#$ and $\Delta\mu_2^\#$ values are positive 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. Other activation parameters i.e. $\Delta H_1^\#$ and $\Delta S_1^\#$ were obtained from the relations:

$$\Delta\mu_1^\# = \Delta H_1^\# - T\Delta S_1^\# \qquad (9)$$

Considering the activation parameters, the activation Gibbs energy, $\Delta\mu_1^\#$ in the two solvent seems to be closer, which according to Feakin's model (Feakins *et al.*, 1974) that the higher this value is the greater is the structure making ability. Therefore the solute may be said to have similar effect on the solute as regard the structure making with a little variation based on concentration. The values of $\Delta S_1^\#$ obtained suggest that the attainment of transition state for viscous flow is by bond formation. The values of $\Delta H_1^\#$ suggested that additional work is required to dissolve L-Alanine in water than ethanol.

- solute interaction between L-alanine molecules than ionic interactions with the solvent molecules.

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