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Volumetric and Thermodynamic Parameters of l-Leucine in Ethanol+ Water Mixtures at Different Temperatures

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Abstract: Densities and viscosities of L-leucine in aqueous solutions of ethanol (1 to 10 mass %) have been measured at 298.15, 303.15, 308.15, 310.15 and 313.15 K. These data have been used to calculate apparent molar volume, V_{Φ}, limiting apparent molar volume, V_{Φ}^{0} and the slopes, S_v, transfer volumes, $V_{\Phi\,tr}^{0}$, Falkenhagen Coefficient, A and Jones – Dole coefficient, B. These parameters have been used to discuss the solute-solute and solute-solvent interactions in these systems.

Keywords: Viscosity, Density, Partial molar volumes, Viscosity – A and B coefficient

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1. INTRODUCTION

The physicochemical properties of amino acids in aqueous solutions provide valuable information on solute-solute and solute-solvent interactions [1-6]. These interactions are important in understanding the stability of proteins, and are implicated in several biochemical and physiological processes in a living cell [7-9]. A.Ali and Shahajan[10] measured the density and viscosity and refractive index in aqueous tetrapropylammonium bromide containing l-leucine Dl-alanine Dl-valine and glycine for several concentrations of amino acids at different temperatures. A.Ali ,S. Khan and F. Nabi[11] measured the density and viscosity and refractive index in aqueous glycerol containing l-leucine Dl-alanine Dl-valine, Dl-α- amino-n- butyric acid and glycine for several concentrations of amino acids at different temperatures.

In continuation of our earlier work[12,13], in the present article, we report the densities, ρ, viscosities, η, of l-leucine in aqueous ethanol (1 to 10 wt. % of ethanol, w/w in water) at 298.15, 303.15, 308.15, 310.15, and 313.15 K. Experimental data have been used to calculate, apparent molar volume, V_{Φ}, limiting apparent molar volume, V_{Φ}^{0} and the slopes, S_v, transfer volumes, $V_{\Phi tr}^{0}$, Falkenhagen Coefficient, A and Jones – Dole coefficient, B. These parameters have been used to discuss the solute-solute and solute-solvent interactions in these systems.

2. Experimental

Analytical grade l-leucine (Research Lab.) was used as it is without further purification. Ethanol (Research Lab) was distilled using quick fit glass assembly. The aqueous ethanol solutions (1 to 10 wt % of ethanol, w/w in water) were prepared using triple distilled water (conductivity less than

1×10^{-6} S cm^{-1}) and they were used as solvents to prepare l-leucine solutions of eight different molar concentrations (ranging from 0.0154 to 0.0518 M). The weightings were done on an electric one pan balance (Model Dhona 200, India) with a precision of ±0.01 mg .The solutions were prepared with care and stored in special airtight bottles to avoid contamination and evaporation.

The densities of the sample solutions were measured by using a bicapillary pycnometer (made of borosil glass) having a bulb capacity of~ 15 mL. The graduated marks on the capillary were calibrated by using triply distilled water. The accuracy of density measurements was estimated to be $\pm 0.09 \times 10^{-6}$kg m^{-3}. The viscosities of the solutions were measured by using Ubbelohde type suspended level viscometer in similar manner as reported by Nikam et al [13]. The viscometer containing the test liquid was allowed to stand for about 20 minutes in a thermostatic water bath so that the thermal fluctuations in viscometer were minimized. The time of flow was recorded in triplicate with a digital stopwatch with an accuracy of ±0.01 s. The accuracy of viscosity measurements was found to be $\pm 1.7 \times 10^{-6}$ N.s.m^{-2}. The temperature of the test solution during the measurements was maintained to an accuracy of ±0.01K in an electronically controlled thermostatic water bath.

3. Results and Discussion

The experimental values of density, ρ, and viscosity, η of l-leucine solutions in aqueous ethanol solvents as a function of molar concentration and at various temperatures are listed in Table 1 and Table 2 respectively.

3.1 Partial molar volume

The partial molar volume, V_Φ of this solute V_Φ^0 of l-leucine in aqueous ethanol solutions were calculated by using the relations

$$V_\Phi = \frac{1000(\rho_0 - \rho)}{C\rho_0\rho} + \frac{M}{\rho} \tag{1}$$

where C is the molar concentration of l-leucine, ρ and ρ_0 are the densities of the solution and the solvent (aqueous - ethanol) respectively is the molar mass of

l -isoleucine.

The partial molar volumes, V_Φ, as functions of square root of concentration at various temperatures are shown graphically in Fig.1A.to1E. It is observed that, for l-leucine in all the ten aqueous-ethanol solvents, V_Φ was almost linear in the studied concentration range and at each investigated temperature.

3.2 Limiting partial molar volume

The values of limiting partial molar volume, V_Φ^0 and the slope, S_v, have been obtained using method of linear regression of V_Φ vs. molar concentration (C) of l-leucine in ethanol- water solvents from the following relation[14].

$$V_\Phi = V_\Phi^0 + S_v C \tag{2}$$

Where the intercepts, V_Φ^0 by definition are free from solute-solute interactions and therefore provide a measure of solute-solvent interactions, whereas the experimental slope, S_v, provides information regarding solute-solute interaction. The values of V_Φ^0, and S_v for l-leucine in aqueous – ethanol solutions at different temperatures are listed in Table 3.

A close perusal of Table 3 reveals that the V_{Φ}^{0} and S_v values are positive for l-leucine in aqueous-ethanol solutions indicating the presence of strong solute – solvent interactions and strong solute – solute interactions respectively in the solvent systems under investigation. The trends observed in V_{Φ}^{0} values can be due to their hydration behavior[15-19], which comprises of the following interactions in the present solvent: (a) The terminal groups of zwitterions of amino acids, $NH^{+}{}_{3}$ and COO^{-} are hydrated in an electrostatic manner whereas, hydration of R group depends on its nature, which may be hydrophilic, hydrophobic or amphiphilic; and (b) the overlap of hydration co-spheres of terminal $NH^{+}{}_{3}$ and COO^{-} groups and of adjacent groups results in volume change. The V_{Φ}^{0} values increase due to reduction in the electrostriction at terminals, whereas it decreases due to disruption of side group hydration by that of the charged end.

The increase in V_{Φ}^{0} values with increase in temperature for l-leucine in aqueous-ethanol solutions can be explained by considering the size of primary and secondary solvation layers around the zwitterions. At higher temperatures the solvent from the secondary solvation layer of l-leucine zwitterions is released into the bulk of the solvent, resulting in the expansion of the solution, as inferred from larger V_{Φ}^{0}

Table 1 Densities, ρ, of solutions of l - leucine in ethanol + water (1 to 10 % ethanol, w/w in water) solvents as a functions of molar concentration of l - leucine in ethanol + water and at various temperatures.

C/ mol kg^{-1}	density, ρ, kg. m^{-3}					density, ρ, kg. m^{-3}				
	Temperature K					Temperature K				
	298.15	303.15	308.15	310.15	313.15	298.15	303.15	308.15	310.15	313.15
1% ethanol						2% ethanol				

0.0154	995.27	993.99	992.48	992.07	990.63	993.28	991.85	988.52	987.84	987.52
0.0179	995.30	994.02	992.51	992.10	990.66	993.31	991.88	988.55	987.87	987.55
0.0208	995.34	994.06	992.55	992.14	990.70	993.35	991.92	988.59	987.91	987.59
0.0240	995.38	994.10	992.59	992.18	990.74	993.39	991.96	988.63	987.95	987.63
0.0257	995.40	994.12	992.61	992.21	990.77	993.43	991.98	988.65	987.97	987.65
0.0320	995.49	994.20	992.70	992.29	990.85	993.49	992.06	988.73	988.05	987.74
0.0399	995.59	994.31	992.80	992.39	990.95	993.60	992.17	988.84	988.16	987.84
0.0518	995.75	994.47	992.96	992.55	991.11	993.76	992.33	989.00	988.32	988.00
3% ethanol						4% ethanol				
0.0154	991.73	990.36	988.82	988.18	987.08	989.99	988.62	987.04	986.32	985.36
0.0179	991.76	990.40	988.86	988.21	987.12	990.02	988.65	987.07	986.36	985.40
0.0208	991.80	990.43	988.89	988.24	987.15	990.06	988.69	987.11	986.39	985.43
0.0240	991.84	990.47	988.93	988.28	987.19	990.10	988.73	987.15	986.43	985.47
0.0257	991.86	990.50	988.96	988.31	987.22	990.12	988.75	987.17	986.45	985.49
0.0320	991.95	990.58	989.04	988.39	987.30	990.20	988.83	987.25	986.54	985.58
0.0399	992.05	990.68	989.14	988.49	987.40	990.31	988.94	987.36	986.64	985.68
0.0518	992.21	990.84	989.30	988.65	987.56	990.47	989.10	987.52	986.80	985.84
5% ethanol						6% ethanol				
0.0154	988.46	987.00	985.00	984.75	983.59	985.49	983.93	982.80	981.91	981.05
0.0179	988.49	987.03	985.03	984.79	983.63	985.52	983.96	982.83	981.94	981.08
0.0208	988.53	987.07	985.07	984.82	983.66	985.55	983.99	982.87	981.98	981.12
0.0240	988.57	987.11	985.11	984.86	983.70	985.60	984.04	982.91	982.02	981.16
0.0257	988.59	987.13	985.13	984.88	983.72	985.62	984.06	982.93	982.04	981.18
0.0320	988.67	987.21	985.21	984.96	983.80	985.70	984.14	983.01	982.12	981.26

0.0399	988.78	987.31	985.32	985.07	983.91	985.80	984.25	983.11	982.22	981.36
0.0518	988.94	987.48	985.48	985.23	984.07	985.96	984.40	983.27	982.38	981.52
7% ethanol						8% ethanol				
0.0154	985.18	983.77	982.04	981.28	980.12	982.57	981.14	979.30	978.52	977.69
0.0179	985.22	983.80	982.07	981.31	980.15	982.60	981.18	979.33	978.55	977.72
0.0208	985.23	983.83	982.10	981.35	980.19	982.64	981.21	979.37	978.58	977.75
0.0240	985.29	983.87	982.14	981.38	980.22	982.68	981.25	979.41	978.62	977.79
0.0257	985.31	983.89	982.16	981.41	980.25	982.70	981.27	979.43	978.64	977.81
0.0320	985.39	983.97	982.24	981.49	980.33	982.78	981.35	979.51	978.72	977.89
0.0399	985.50	984.08	982.35	981.59	980.43	982.88	981.45	979.62	978.83	978.00
0.0518	985.66	984.24	982.51	981.75	980.59	983.04	981.61	979.78	978.99	978.16
9% ethanol						10% ethanol				
0.0154	982.22	980.84	979.02	978.26	977.05	979.48	978.26	976.74	976.13	974.74
0.0179	982.25	980.87	979.06	978.29	977.08	979.51	978.29	976.77	976.17	974.77
0.0208	982.29	980.91	979.09	978.32	977.11	979.54	978.33	976.81	976.20	974.80
0.0240	982.33	980.95	979.13	978.36	977.15	979.58	978.37	976.85	976.24	974.84
0.0257	982.35	980.97	979.15	978.38	977.17	979.60	978.39	976.87	976.26	974.86
0.0320	982.43	981.05	979.23	978.46	977.25	979.68	978.47	976.95	976.34	974.94
0.0399	982.53	981.15	979.33	978.56	977.36	979.78	978.57	977.05	976.44	975.04
0.0518	982.69	981.31	979.50	978.73	977.52	979.94	978.72	977.21	976.60	975.21

values at higher temperatures[20,21]. Similar trends in V_{Φ}^{0} values were obtained by .li, S. Khan and F. Nabi [11] on interactions of l-leucine in aqueous solution of glycerol.

3.3 Transfer volume

Limiting apparent molar properties of transfer volume V^0_Φ provide qualitative as well as quantitative information regarding solute-solvent interactions without taking into account the effects of solute – solute interactions [22]. The transfer volumes, $V^0_{\Phi\,tr}$ of l-leucine from water to aqueous – ethanol solutions were calculated by using the relation

$$V^0_{\Phi\,tr} = V^0_{\Phi aq.ethanol} - V^0_{\Phi,\,water} \quad (3)$$

Where, $V^0_{\varphi,\,water}$, is the limiting apparent molar volume of l-leucine in water. The $V^0_{\Phi\,,tr}$ values for l-leucine from water to aqueous ethanol solutions are included in Table 4. Transfer volumes, $V^0_{\Phi\,tr}$ values of l-leucine are positive as well as negative. In general, the types of interactions occurring between l-leucine and ethanol can be classified as follows [11,22,23]

(a) The hydrophilic – ionic interaction between OH groups of ethanol and zwitterions of l- leucine.

(b) Hydrophilic – hydrophilic interaction the OH groups of ethanol and NH groups in the side chain of acid l-leucine through hydrogen bonding.

(c) Hydrophilic – hydrophobic interaction between the OH groups of ethanol molecule and non- polar (-CH_2) in the side chain of l-leucine molecule.

(d) Hydrophobic – hydrophobic group interactions between the non- polar groups of ethanol and non – polar (-CH_2) in the side chain of l-leucine molecule.

The $V^0_{\Phi\,tr}$ values decrease due to disruption of side group hydration by that of the charged end by negative contribution from the interactions of type (c) and (d) mentioned earlier. The observed positive $V^0_{\Phi\,tr}$ values upto 0.0119 mole fraction of ethanol suggest that the hydrophilic – ionic group and hydrophilic – hydrophilic group interactions dominate in these systems. The $V^0_{\Phi\,tr}$ values decrease with increase in ethanol concentration in the solutions. This may be due to greater Hydrophilic – hydrophobic groups and Hydrophobic – hydrophobic group interactions with increased concentrations of ethanol. The similar trends in V^{0}_{Φ} and $V^{0}_{\Phi tr}$ with sucrose concentration were also observed by Zhao et al.[4] from volumetric properties of arginine in aqueous-carbohydrate solutions at 298.15K.

4. Analysis of viscosity data

The viscosity data were analysed by using Jones – Dole [24] equation of the form

$$\eta_r = \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \qquad (4)$$

Where η_r is the relative viscosity of the solution, η and η_0 are the viscosities of solution and the solvent (ethanol + water), respectively, C is the molar concentration of l-leucine in ethanol + water solvent, A and B are the Falkenhagen [25,26]and Jones – Dole [24] coefficients, respectively.

Table 2 Viscosities, η, N.s.m^{-2} of solutions of l - leucine in ethanol + water (1 to 10 % ethanol, w/w in water) solvents as a functions of molar concentration of l - leucine in ethanol + water and at various temperatures.

C/ mol kg^{-1}	Viscosity, η ,					Viscosity, η ,				
	Temperature K					Temperature K				
	298.15	303.15	308.15	310.15	313.15	298.15	303.15	308.15	310.15	313.15
1% ethanol						2% ethanol				
0.0154	0.9200	0.8280	0.7462	0.7169	0.6790	0.9571	0.8459	0.7651	0.7326	0.6948
0.0179	0.9230	0.8309	0.7491	0.7199	0.6816	0.9601	0.8489	0.7680	0.7355	0.6977
0.0208	0.9262	0.8340	0.7523	0.7230	0.6848	0.9633	0.8521	0.7712	0.7387	0.7009
0.0240	0.9297	0.8370	0.7557	0.7264	0.6882	0.9667	0.8555	0.7746	0.7421	0.7044
0.0257	0.9314	0.8387	0.7577	0.7283	0.6902	0.9685	0.8576	0.7766	0.7440	0.7065

0.0320	0.9375	0.8448	0.7638	0.7344	0.6963	0.9746	0.8640	0.7827	0.7501	0.7127
0.0399	0.9457	0.8529	0.7719	0.7425	0.7045	0.9821	0.8725	0.7908	0.7582	0.7208
0.0518	0.9557	0.8630	0.7824	0.7541	0.7153	0.9919	0.8862	0.8012	0.7680	0.7317
3% ethanol						4% ethanol				
A0.0154	0.9903	0.8695	0.7616	0.7521	0.7180	1.0335	0.9052	0.8125	0.7738	0.7368
0.0179	0.9933	0.8724	0.7645	0.7550	0.7210	1.0364	0.9082	0.8154	0.7767	0.7399
0.0208	0.9965	0.8756	0.7676	0.7581	0.7243	1.0397	0.9114	0.8187	0.7798	0.7431
0.0240	1.0000	0.8791	0.7711	0.7615	0.7277	1.0431	0.9148	0.8223	0.7832	0.7466
0.0257	1.0017	0.8809	0.7730	0.7636	0.7298	1.0449	0.9166	0.8242	0.7853	0.7487
0.0320	1.0075	0.8869	0.7791	0.7696	0.7360	1.0510	0.9226	0.8303	0.7914	0.7548
0.0399	1.0142	0.8954	0.7872	0.7778	0.7443	1.0585	0.9307	0.8385	0.7996	0.7632
0.0518	1.0234	0.9062	0.7976	0.7885	0.7551	1.0685	0.9406	0.8495	0.8103	0.7739
5% ethanol						6% ethanol				
0.0154	1.0777	0.9491	0.8611	0.8050	0.7534	1.1198	0.9773	0.8651	0.8189	0.7670
0.0179	1.0815	0.9520	0.8641	0.8077	0.7547	1.1244	0.9803	0.8681	0.8217	0.7700
0.0208	1.0856	0.9552	0.8674	0.8109	0.7578	1.1289	0.9835	0.8712	0.8246	0.7735
0.0240	1.0899	0.9586	0.8708	0.8144	0.7613	1.1336	0.9869	0.8746	0.8280	0.7773
0.0257	1.0921	0.9606	0.8728	0.8164	0.7633	1.1363	0.9888	0.8766	0.8300	0.7793
0.0320	1.0997	0.9666	0.8789	0.8226	0.7694	1.1445	0.9949	0.8827	0.8360	0.7858
0.0399	1.1084	0.9744	0.8870	0.8309	0.7776	1.1534	1.0026	0.8909	0.8441	0.7943
0.0518	1.1202	0.9844	0.8982	0.8468	0.7896	1.1659	1.0127	0.9016	0.8547	0.8050

Table.2: Continued……..

C mol/kg^{-1}	Viscosity, η ,					Viscosity, η ,				
	Temperature K					Temperature K				
	298.15	303.15	308.15	310.15	313.15	298.15	303.15	308.15	310.15	313.15
7 % ethanol						8 % ethanol				
0.0154	1.1641	0.9733	0.8911	0.8342	0.7879	1.2026	1.0444	0.9191	0.8687	0.8177
0.0179	1.1692	0.9764	0.8940	0.8377	0.7907	1.2076	1.0474	0.9221	0.8717	0.8206
0.0208	1.1747	0.9798	0.8972	0.8411	0.7939	1.2130	1.0505	0.9252	0.8749	0.8237
0.0240	1.1808	0.9834	0.9006	0.8446	0.7974	1.2190	1.0539	0.9287	0.8783	0.8271
0.0257	1.1840	0.9854	0.9025	0.8466	0.7994	1.2221	1.0563	0.9307	0.8804	0.8290
0.0320	1.1946	0.9917	0.9087	0.8538	0.8057	1.2327	1.0628	0.9368	0.8866	0.8350
0.0399	1.2074	0.9993	0.9168	0.8618	0.8141	1.2449	1.0678	0.9450	0.8951	0.8431
0.0518	1.2250	1.0097	0.9275	0.8734	0.8287	1.2619	1.0799	0.9558	0.9059	0.8537
	9 % ethanol					10 % ethanol				
0.0154	1.2491	1.0805	0.9535	0.8983	0.8362	1.3070	1.1101	1.0516	0.9693	0.8614
0.0179	1.2534	1.0846	0.9566	0.9026	0.8386	1.3124	1.1133	1.0549	0.9724	0.8644
0.0208	1.2580	1.0891	0.9600	0.9072	0.8413	1.3195	1.1166	1.0584	0.9756	0.8676
0.0240	1.2628	1.0938	0.9635	0.9121	0.8447	1.3270	1.1202	1.0622	0.9790	0.8711
0.0257	1.2652	1.0963	0.9653	0.9155	0.8467	1.3303	1.1220	1.0642	0.9811	0.8731
0.0320	1.2736	1.1047	0.9717	0.9269	0.8527	1.3438	1.1282	1.0707	0.9873	0.8793
0.0399	1.2842	1.1164	0.9790	0.9372	0.8610	1.3612	1.1354	1.0785	0.9951	0.8860
0.0518	1.2988	1.1299	0.9888	0.9543	0.8719	1.3868	1.1452	1.0890	1.0057	0.8952

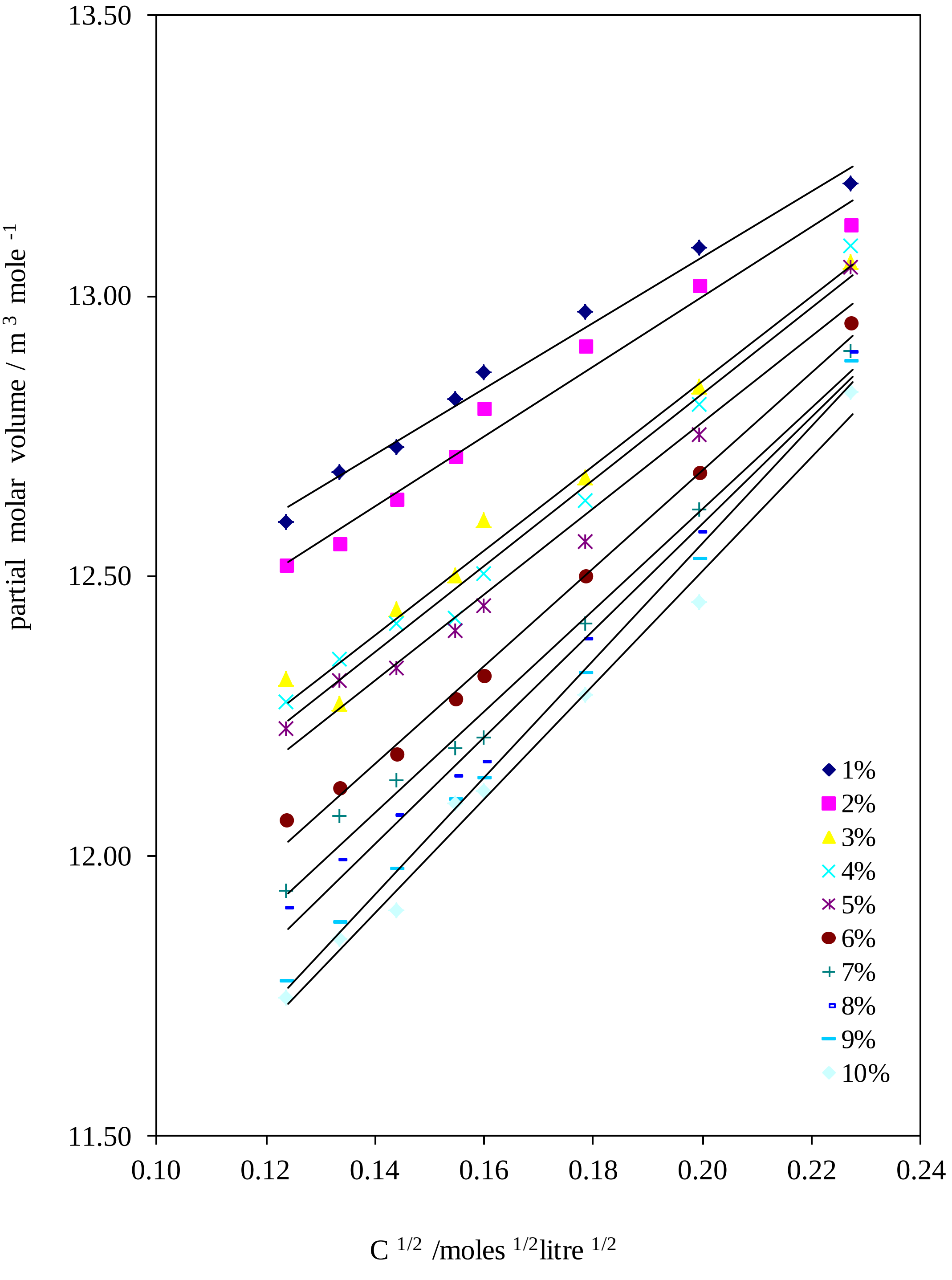


Fig.1.(A). Variation of partial molar volumes, V_{Φ} vs. molar concentration, C of l - leucine in ethanol + water (w/w) solutions at 298.15 K.

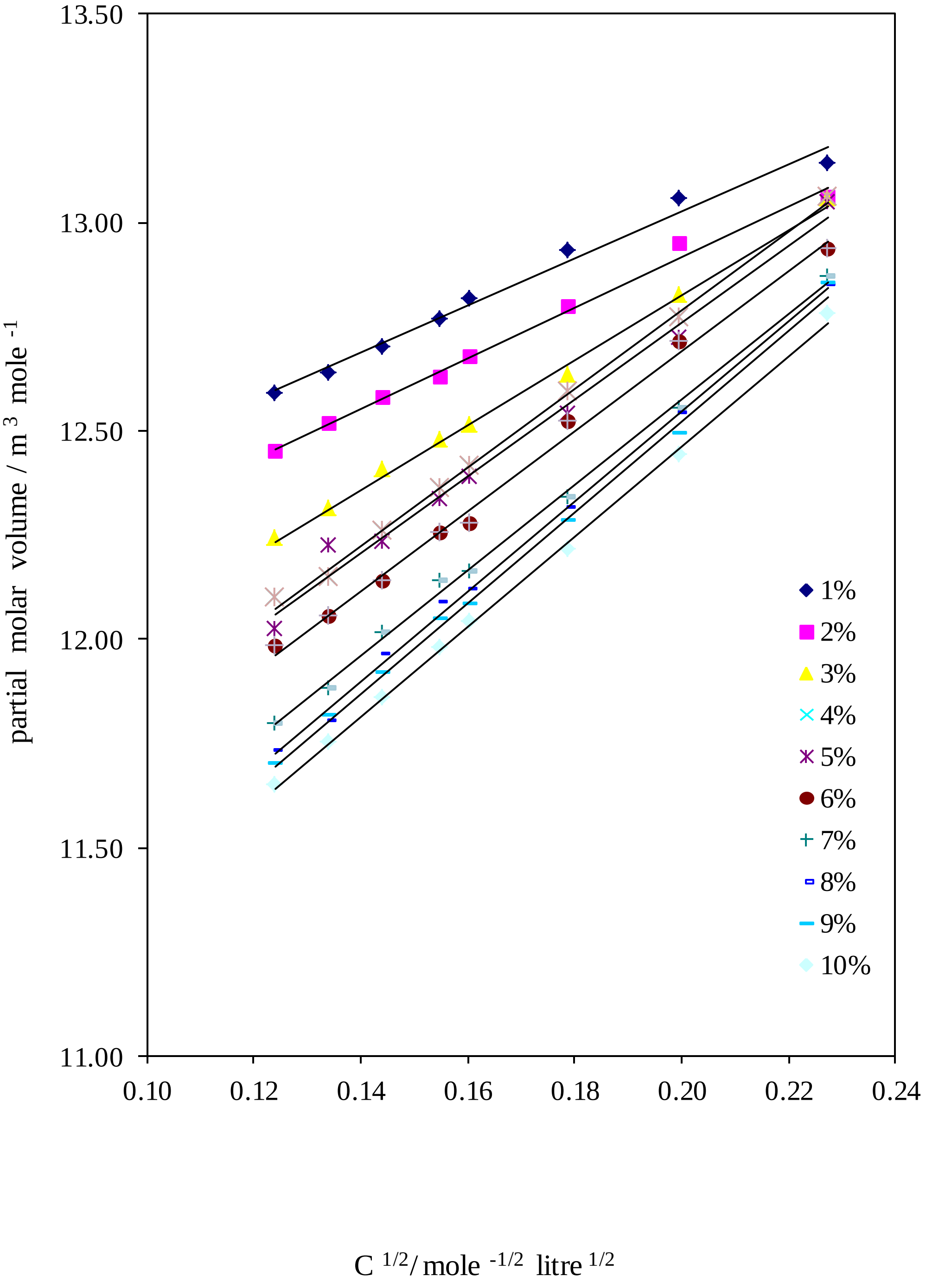
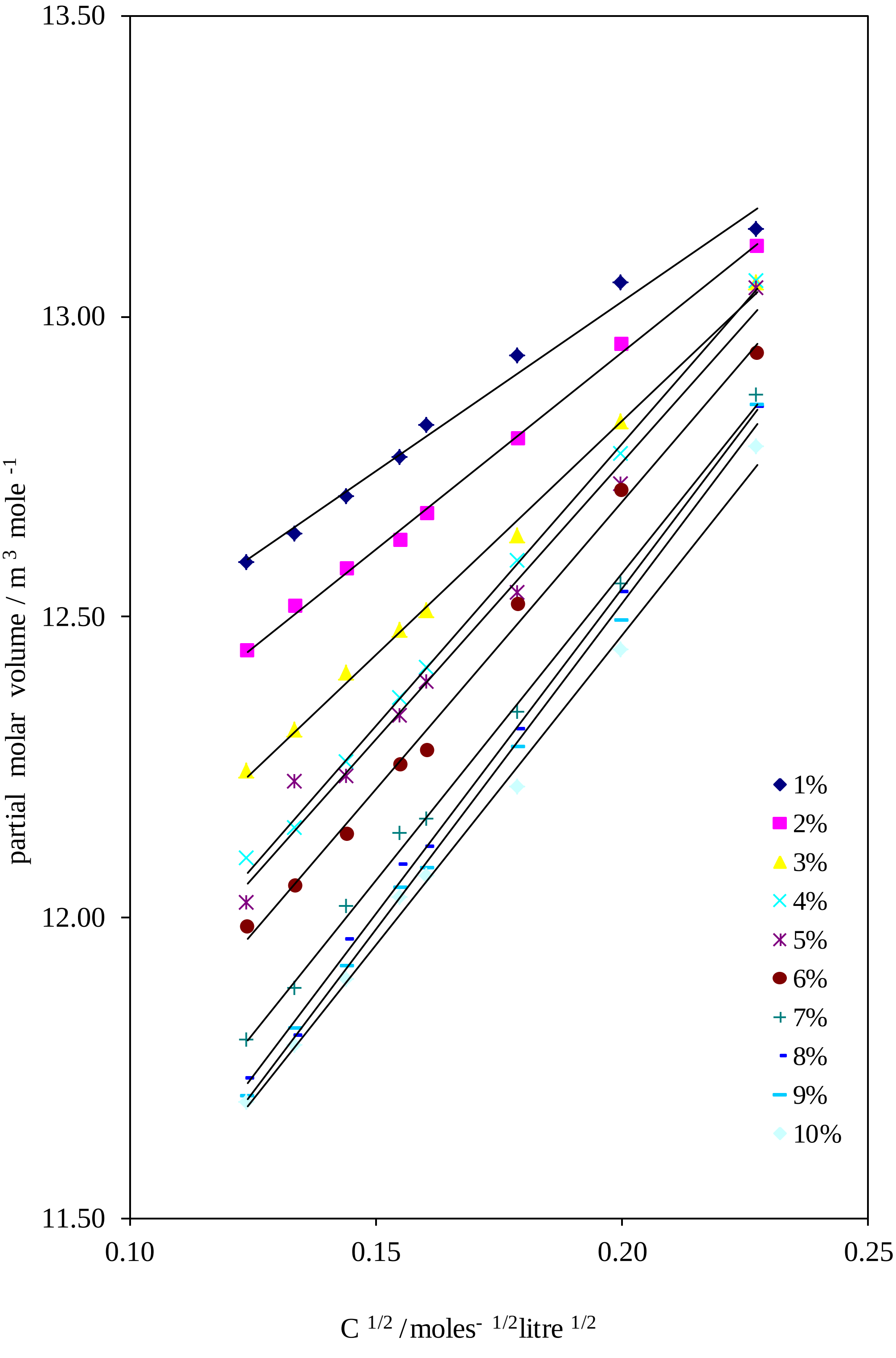


Fig.1. (B). Variation of partial molar volumes, V_Φ vs. molar concentration, C of l - leucine in ethanol + water (w/w) solutions at 303.15 K.



Figi.1 (c). Variation of partial molar volumes,V_Φ vs. molar concentration, C of

l - leucine in ethanol + water (w/w) solutions at 308.15 K.

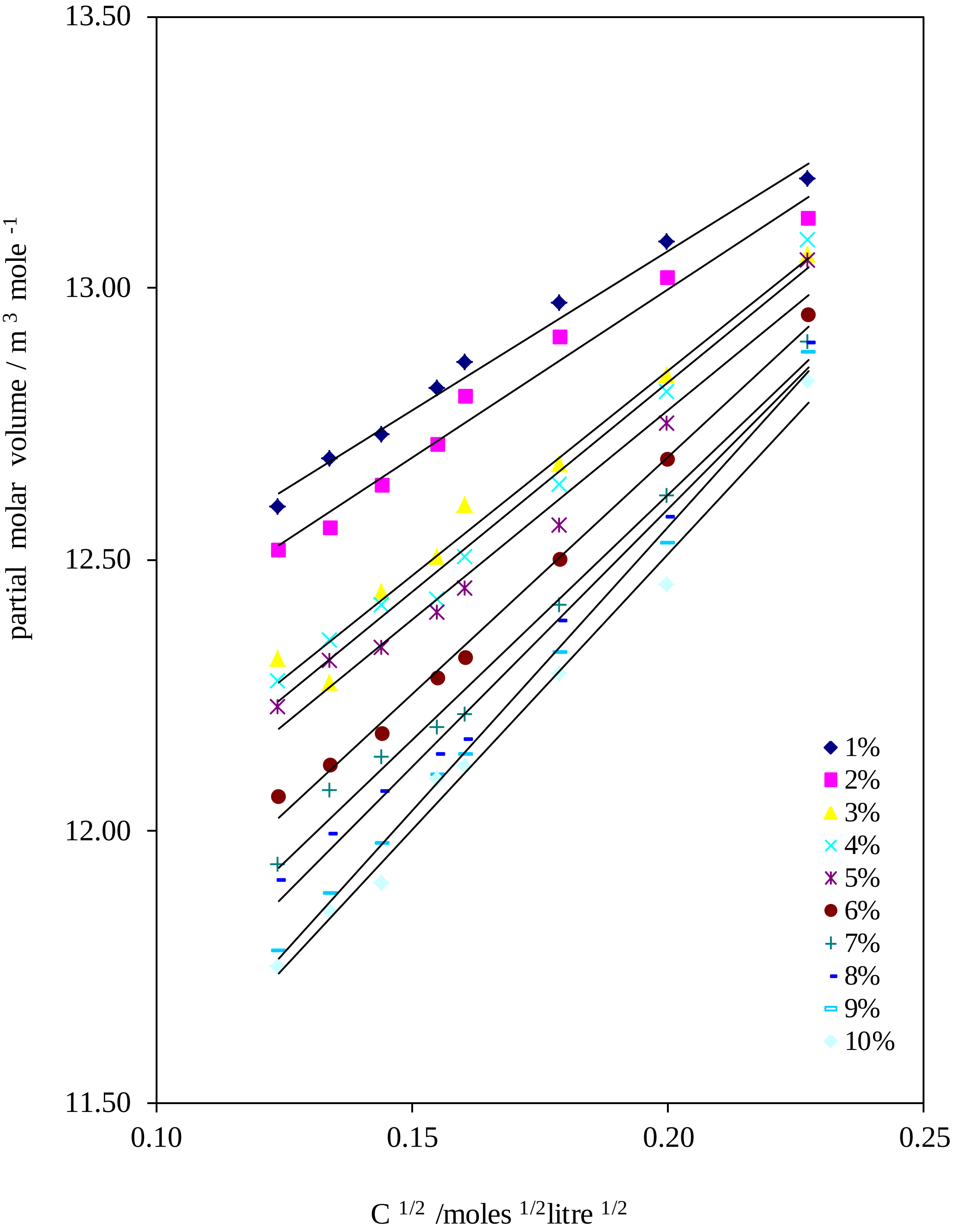


Fig.1 (D). Variation of partial molar volumes, V_{Φ} vs. molar concentration, C of l- leucine in ethanol + water (w/w) solutions at 310.15 K.

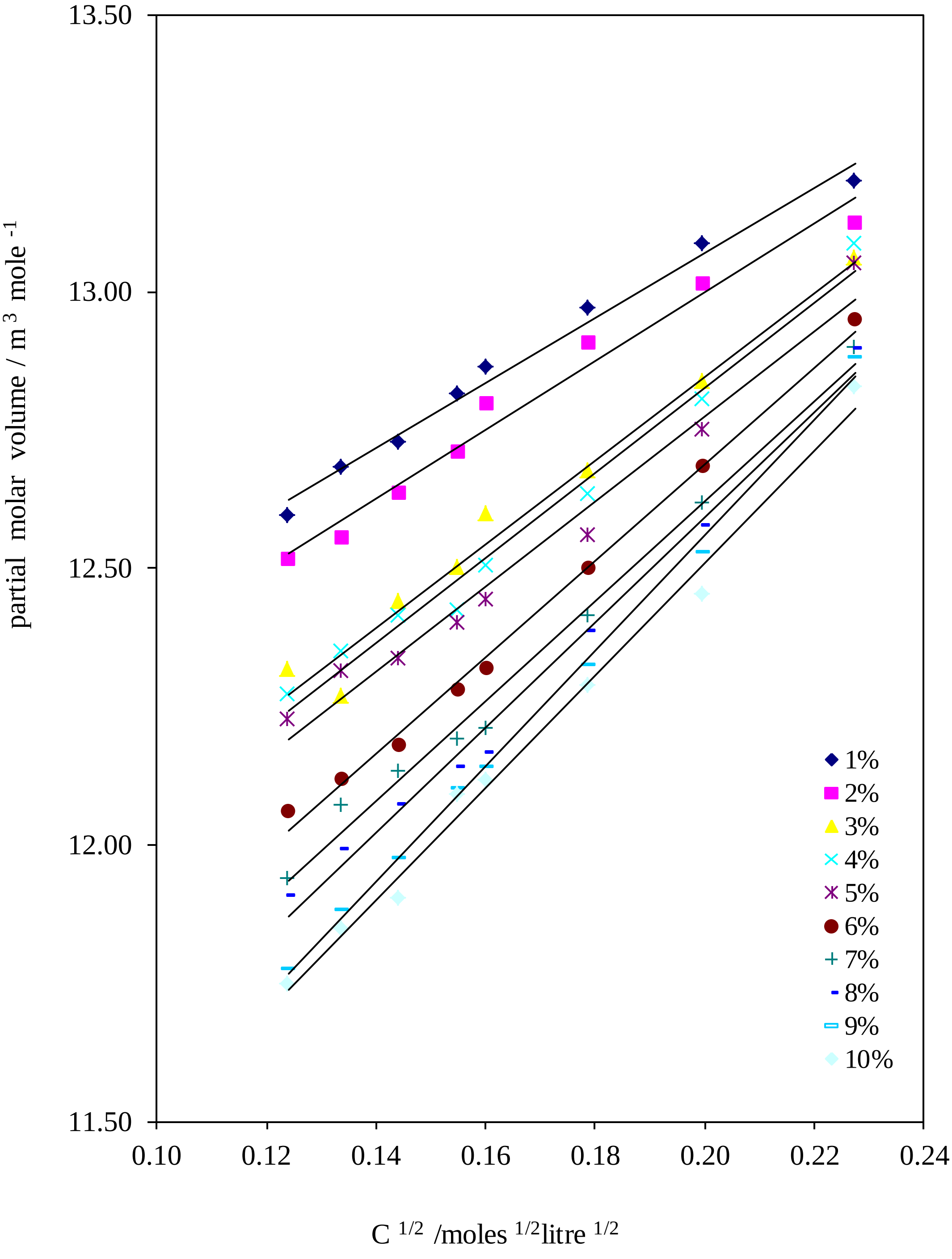


Fig. 1(E). Variation of partial molar volumes, V_Φ vs. molar concentration, C of l - leucine in ethanol + water (w/w) solutions313.15 K.

Table 3. Limiting apparent molar volume, $10^5.V_{\Phi}^{0}$ /m^3 mole^{-1} and slopes, $10^5.S_v$/ m^3 mole^{-1} kg^{-1} in ethanol + water (1 to 10 % ethanol, w/w in water) solvents as a function of concentration, C, of l-isoleucine at various temperatures.

298.15 K		303.15 K		308.15 K		310.15 K		313.15 K	
V_{Φ}^{0}	S_v	V_{Φ}^{0}	S_v	V_{Φ}^{0}	S_v	V_{Φ}^{0}	S_v	V_{Φ}^{0}	S_v
1% ethanol									
10.70	6.665	11.72	6.313	11.89	5.643	11.89	5.884	11.83	6.379
2% ethanol									
10.59	6.740	11.58	6.619	11.63	6.548	11.75	6.223	11.74	6.584
3% ethanol									
10.89	9.593	11.05	8.958	11.27	7.774	11.33	7.560	11.32	7.775
4% ethanol									
10.82	9.856	10.74	10.97	10.90	9.395	11.28	7.706	11.33	7.523
5% ethanol									
10.50	11.21	10.56	9.80	10.91	9.210	11.23	7.705	11.28	7.612
6% ethanol									
10.44	11.18	10.68	9.80	10.77	9.577	10.94	8.739	11.03	8.319
7% ethanol									
10.41	10.52	10.14	10.06	10.52	10.24	10.81	9.037	10.81	9.173
8% ethanol									
10.03	11.73	10.36	11.73	10.38	10.81	10.69	9.508	10.75	9.383
9% ethanol									
10.20	11.25	10.29	10.71	10.32	10.88	10.47	10.44	10.66	9.733
10% ethanol									
10.12	10.41	10.30	10.14	10.37	10.40	10.47	10.16	10.63	9.387

Table 3. Transfer volume, $V^{0}_{\Phi\ tr}$ for l - leucine in aqueous ethanol at different temperatures.

Mole fraction of ethanol	$V^{0}_{\Phi\ tr}$ / $m^3\ mol^{-1}$				
	Temperature K				
	298.15	303.15	308.15	310.15	313.15
0.0039	0.02	-0.02	0.04	-0.02	-0.01
0.0079	-0.08	-0.11	-0.19	-0.24	-0.14
0.0119	-0.54	-0.46	-0.41	-0.43	-0.44
0.016	-0.74	-0.61	-0.62	-0.50	-0.47
0.0201	-0.75	-0.71	-0.66	-0.54	-0.55
0.0243	-0.93	-0.73	-0.76	-0.72	-0.71
0.0285	-1.07	-0.94	-0.94	-0.88	-0.81
0.0328	-1.08	-1.00	-1.04	-0.52	-0.89
0.0372	-1.21	-1.07	-0.64	-1.07	-0.94
0.0416	-1.24	-1.12	-1.04	-1.10	-1.02

Table 4 Parameters of Jones – Dole equation B, dm^3 mole^{-1} and A, dm^3 mole$^{-½}$ for l - leucine in Water + Ethanol mixtures at different temperatures.

298.15 K		303.15 K		308.15 K		310.15 K		313.15 K	
B	A	B	A	B	A	B	A	B	A
1% ethanol									
0.3670	-0.2186	0.3638	-0.0761	0.3669	-0.078	0.3382	-0.0128	0.3650	-0.0101
2% ethanol									
0.3636	-0.3908	0.3579	-0.2338	0.3556	-0.1012	0.3556	-0.1174	0.3686	-0.1486
3% ethanol									
0.3543	-0.9754	0.3579	-0.6136	0.3643	-0.4826	0.3626	-0.0425	0.3537	-0.0628
4% ethanol									
0.3631	-0.1976	0.3582	-0.1194	0.3813	-0.1827	0.3600	-0.1152	0.3638	-0.0530
5% ethanol									
0.3584	-0.4132	0.3648	-0.0542	0.2753	-0.3062	0.3498	-0.0358	0.3739	-0.1365
6% ethanol									
0.3719	-0.6262	0.3537	-0.1426	0.3851	-0.4349	0.3621	-0.3924	0.3706	-0.3624
7% ethanol									
0.3602	-0.3782	0.4603	-0.4266	0.3537	-0.3155	0.3624	-0.3742	0.3584	-0.3850
8% ethanol									
0.3644	-0.4107	0.3581	-0.1054	0.3585	-0.0480	0.4216	-0.2692	0.3997	-0.0698
9% ethanol									
0.4172	0.0394	0.4767	-0.4190	0.3675	-0.0390	0.3615	-0.3594	0.3452	-0.4795
10% ethanol									
0.3723	0.0115	0.5589	-0.1426	0.3521	-0.0447	0.3743	-0.0806	0.3542	-0.4121

Coefficient 'A' accounts for the solute – solute interactions and B is a measure of structural modifications induced by the solute – solvent interactions[27,28]. The values of A and B have been obtained as the intercept and slope from linear regression of $[(\eta_r - 1)/ C^{1/2}]$ Vs. $C^{1/2}$ curves, which were found almost linear for this

systems. The values of A and B are listed in Table 5. The values of A-coefficients are negative while that of B-coefficients are positive. The A- coefficients are much smaller in magnitude as compared to B-coefficients, suggesting weak solute- solute and solute-solvent interactions in these solutions. Positive B-coefficients values, which increase with increasing concentration of ethanol, also indicate a structure to allow the co – solute (ethanol) to act on solvent[1].

B - Coefficients increase when the water is replaced by ethanol, i.e., ethanol acts as water structure – maker by H-bonding. B-coefficients increases with increasing concentration of ethanol, the reason may be that the friction increases to prevent water flow at increased ethanol concentration.

5. Hydration number

The value of hydration numbers (N_h) reflects the electrostriction effect of the charge centre of the amino acids on the nearby water molecules. The hydration numbers of amino acids in aqueous ethanol solutions were estimated using the method reported by Shahidi et al [29] and are included in Table 6.

$$V^{0}_{\Phi\, tr} = [N_h \text{ (in water)} - N_h \text{ (in ethanol solution)}] \times 3 \qquad (5)$$

According to Millero et al [9], the hydration number of amino acid in water can be evaluated by the following equation,

$$N_h \text{ (in water)} = \frac{V_{elect}}{V^{0}_{e} - V^{0}_{b}} \qquad (6)$$

where V_{elect} is the molar mass of electrostricted water and V^{0}_{b} is the molar volume of bulk water. The value of $V^{0}_{e} - V^{0}_{b}$ is approximately 3.3 cm^3 mol^{-1}. The electrostriction partial molar volume (V_{elect}) can be estimated from the measured V^{0}_{Φ} value of the amino acid using the following equation.

$$V^{0}_{elect} = V^{0}_{\Phi} - V^{0}_{inter} \tag{7}$$

The intrinsic molar volume V^{0}_{inter} of the amino acid can be estimated from the crystal volume (V^{0}_{cryst}) and the crystal volume can be calculated from the density of the dry-state amino acid[30].

$$V^{0}_{int} = \frac{0.7}{0.634} V^{0}_{cryst} \tag{8}$$

The hydration numbers decrease with the increasing ethanol concentration, which again indicates that the increase in solute-co solute interactions reduces the electrostriction effect of the amino acids. It also suggests that ethanol has a dehydration effect on the l-leucine under investigation. On comparison with the N_h values for the amino acids in ethanol solutions, it can be concluded that ethanol has a little large dehydration effect on the L- isoleucine.

3.6 The free energy of activation per mole of the solvent

The free energy of activation per mole of the solvent ($\Delta \mu_{1}^{0*}$), and the free energy of activation per mole of the solute ($\Delta \mu_{2}^{0*}$) were calculated[27] from the equation 9 and 10.

Table 6: Hydration number for l - leucine in mole fraction of ethanol at different temperatures.

Mole fraction of ethanol	298.15 K.	303.15 K	308.15 K	310.15 K	313.15 K
0.0039	3.39	3.39	3.47	3.46	3.46
0.0079	3.34	3.36	3.32	3.31	3.39
0.0119	3.06	3.12	3.22	3.25	3.24
0.016	2.93	3.03	3.08	3.21	3.23
0.0201	2.94	2.99	3.06	3.20	3.19
0.0243	2.83	2.99	3.02	3.11	3.10
0.0285	2.80	2.90	2.93	3.01	3.06
0.0328	2.81	2.87	2.87	2.99	3.01
0.0372	2.75	2.85	2.86	2.90	2.98
0.0416	2.80	2.86	2.90	2.90	2.95

$$\Delta \mu_1^{0*} = RT \ln \left(\frac{\eta_0 \overline{V}_1^0}{hN} \right) \quad \text{....9}$$

$$\Delta \mu_2^{0*} = \Delta \mu_1^{0*} + \frac{RT}{V_1^0 [1000B - (V_1^0 - V_2^0)]} \quad \text{....10}$$

Where h is planks constant N is Avogadro's number, η_0 is the viscosity of solvent and the other symbols have their usual meanings. The values of $\Delta\mu_1^{0*}$, $\Delta\mu_2^{0*}$, V_1^0 and V_2^{0*} calculated at different temperatures are given in table 7.

It is clear from table 7 that the values of $\Delta\mu_2^{0*}$ are positive and larger than $\Delta\mu_1^{0*}$ indicating a stronger solute-solvent interactions suggesting that the formation of the transition state is less favored in the presence of l - leucine, meaning thereby the formation of transition state is accompanied by the rupture and the distortion of the intermolecular bonds in solvent structure. This feature is similar to that observed for aqueous glycine solution of transition metal chloride[31], or 1-4 dioxanes[7]. According to Feakin's model, the greater the value of $\Delta\mu_2^{0*}$, greater is the structure making ability of the solute. A close perusal of table.7 shows that $\Delta\mu_2^{0*}$ values increase with composition and decrease with temperature. At low mass % ethanol $\Delta\mu_2^{0*}$ values of l-leucine are lower, showing structure breaking tendency.

The activation energy (ΔS_2^{0*})* for l - leucine has been calculated [32] from the relationship in as given by

$$\frac{d\,\Delta\mu_2^{0*}}{dT} = -\Delta S_2^{0*} \qquad \text{....11}$$

Table 7: Values of V_1^0 x10^{-6} / m^3 mol^{-1}, V_2^0 x10^6/ m^3 mol^{-1}, $\Delta\mu_1^{0*}$ /kJ mol^1, $\Delta\mu_2^{0*}$ / kJ mol^{-1} of l - leucine in aqueous ethanol solutions at 298.15, 303.15, 308.15, 310.15 and 313.15 K.

Mass% ethanol	Temperature K	V_1^0	V_2^0	$\Delta\mu_1^{0*}$	$\Delta\mu_2^{0*}$
1	298.15	1.8137	12.26	43.43	60.92
	303.15	1.838	12.27	43.90	59.73
	308.15	1.8262	12.38	44.37	58.89
	310.15	1.8301	44.37	44.56	58.53
	313.15	1.8508	12.42	44.98	58.20
2	298.15	1.8371	12.17	43.50	61.84
	303.15	1.8402	12.15	43.99	60.43
	308.15	1.8427	12.19	44.44	59.47
	310.15	1.8466	12.29	44.63	59.01
	313.15	1.8912	12.35	44.98	59.50
3	298.15	1.8531	11.71	43.65	62.81
	303.15	1.8635	11.82	44.00	61.11
	308.15	1.8591	11.93	44.54	59.66
	310.15	1.8629	11.99	44.73	59.58
	313.15	1.9315	11.99	45.11	59.50
4	298.15	1.8696	11.53	43.78	64.01
	303.15	1.8732	11.66	44.19	62.23
	308.15	1.8759	11.75	44.64	60.92
	310.15	1.8798	11.92	44.83	60.28
	313.15	1.9729	11.95	45.27	60.08
5	298.15	1.8860	11.45		64.99
	303.15	1.8901	11.57	43.89	63.37
	308.15	1.8927	11.69		62.10
	310.15	1.8965	11.88	44.33	61.12
	313.15	2.0143	11.92		60.48
				44.81	
				44.98	

				45.37	
6	298.15	1.9083	11.39	44.00	66.12
	303.15	1.9071	11.52	44.42	64.09
	308.15	1.9100	11.58	44.85	62.33
	310.15	1.9139	11.65	45.03	61.67
	313.15	2.0567	11.79	45.50	61.16
7	298.15	1.9197	1.9197	44.113	67.29
	303.15	1.9243	11.34	44.4	64.27
	308.15	1.9272	11.39	44.96	63.20
	310.15	1.9311	11.57	45.14	62.15
	313.15	2.0991	11.59	45.63	61.79
8	298.15	1.9370	11.16	44.21	68.24
	303.15	1.9419	11.27	44.63	66.03
	308.15	1.9449	11.30	45.07	63.93
	310.15	1.9488	11.49	45.24	63.05
	313.15	2.1425	11.50	45.76	62.60
9	298.15	1.9546	11.03	44.36	69.61
	303.15	1.9598	11.20	44.78	66.91
	308.15	1.9630	11.27	45.15	64.68
	310.15	1.9668	11.35	45.33	63.65
	313.15	2.1869	11.49	45.87	63.11
10	298.15	1.9724	11.01	44.49	70.97
	303.15	1.9770	11.19	44.84	67.91
	308.15	1.9810	11.29	45.43	67.18
	310.15	1.9849	11.34	45.53	65.61
	313.15	2.2324	11.36	46.00	63.91

The values of ΔS_2^{0*} have been calculated from the slopes of linear plots of $\Delta\mu_2^{0*}$ against T. The activation enthalpy (ΔH_2^{0*}) has been calculated from the following equation.

$$\Delta H_2^{0*} = \Delta \mu_2^{0*} + T \Delta S_2^{0*} \qquad \ldots 12$$

The values of $T\Delta S_2^{0*}$ and ΔH_2^{0*} at different temperatures are recorded in table.8.

It is evident from table 8 that entropy of activation is negative, indicating that the formation of transition state is associated with the bond making and a decrease in order. The ΔH_2^{0*} values in 1 and 2 % ethanol are positive suggesting the formation of activated species necessary for viscous flow appears difficult in these solutions [33].

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Table 8: Entropy, $T\Delta S_2^{0*}$ /kJ mol^{-1} and enthalpy ΔH_2^{0*} / kJ mol^{-1}of activation of l –leucine in aqueous ethanol solutions at 298.15, 303.15, 308.15, 310.15 and 313.15 K.

Mass% ethanol		298.15 K	303.15 K	308.15 K	310.15K	313.15 K
1	$T\Delta S_2^{0*}$	-54.26	-55.17	-56.08	-56.45	-56.99
	ΔH_2^{0*}	6.66	4.56	2.80	2.08	1.21
2	$T\Delta S_2^{0*}$	-51.88	-52.75	-53.62	-53.97	-54.49
	ΔH_2^{0*}	9.96	7.68	5.85	5.04	5.01

3	$T\Delta S_2^{0*}$	-86.87	-70.03	-71.18	-71.65	-72.34
	ΔH_2^{0*}	-6.06	-8.92	-11.52	-11.06	-12.83
4	$T\Delta S_2^{0*}$	-80.50	-81.85	-83.20	-83.74	-84.55
	ΔH_2^{0*}	-16.49	-19.62	-22.28	-23.46	-24.47
5	$T\Delta S_2^{0*}$	-90.33	-91.85	-93.37	-93.98	-94.88
	ΔH_2^{0*}	-25.35	-28.48	-83.20	-32.85	-34.40
6	$T\Delta S_2^{0*}$	-101.07	102.77	-104.16	-105.14	-106.15
	ΔH_2^{0*}	-34.95	-38.68	-42.13	-43.47	-44.99
7	$T\Delta S_2^{0*}$	-107.63	-109.43	-111.24	-111.96	-113.05
	ΔH_2^{0*}	-40.34	-45.16	-48.04	-49.81	-51.26
8	$T\Delta S_2^{0*}$	-116.57	-118.53	-120.49	-121.27	-122.44
	ΔH_2^{0*}	-48.34	-52.50	-56.55	-58.22	-59.84
9	$T\Delta S_2^{0*}$	-131.48	-133.69	-135.89	-136.78	-138.09
	ΔH_2^{0*}	-61.67	-66.78	-71.21	-73.72	-74.98
10	$T\Delta S_2^{0*}$	-129.70	-131.87	-134.05	-134.92	-136.22
	ΔH_2^{0*}	-58.72	-63.96	-66.86	-89.30	-72.31

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