THERMODYNAMIC AND ULTRASONIC STUDY OF L-VALINE IN AQUEOUS POTASSIUM CHLORIDE SALT

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Abstract

The experimentally measured parameters like density (ρ), viscosity (η) and ultrasonic velocity (u) of L-Valine of different concentrations in 2% of KCl solutions have been measured at different temperatures. These parameters were used to calculate thermodynamic parameters like adiabatic compressibility (β_a), intermolecular free length (L_f), acoustic impedance (Z), internal pressure (π_i), relaxation time (τ), Gibb's free energy (ΔG), Rao's constant (R), Wada's constant (W) and molecular radius (ro).The study of these parameters shows the existence of intermolecular interaction in the present system.

Keywords: L-Valine, Ultrasonic velocity, thermodynamic parameters, inter molecular interactions

INTRODUCTION

The study of interactions such as hydrogen bonding, electrostatic interactions,and hydrophobic interaction of proteins with salt is important since it explains the conformational stability and unfolding behavior of globular proteins. But proteins are complex molecules of large molecular weights. Hence their direct study is difficult and tedious. Hence study of such the interactions in the systems of amino acids and peptides can be done to reducecomplexity and also it requires less complex measurements techniques [1]. Physicochemical properties of amino acids in aqueous and aqueous electrolytes media finds variety of application in various fields of sciences [2].

L-Valine is an essential non- proteinogenic amino acidwhich helps to remove extra nitrogen from liver and also stimulate muscle growth and the central nervous system. It helps in repairing damaged tissues, promotes normal growth and provides energy to cells. It regulates blood sugar level. It is non-polar in nature and found inside a protein structure to protect it from water. Deficiency of L-valine causes degenerative nerve diseases. Some of the studies on interaction of Valine in aqueous electrolytic solutions have been carried by few researchers [3-5].

MATERIALS AND METHODS

The compound L-Valine(purity 99%) CAS No. 72-18-4, molecular weight 117.146 was obtained from HIMEDIA India Ltd and was used as supplied. The digital balance having an accuracy of ±0.1mg was used for the measurement of weights. The fresh L-Valine solutions under the study of different concentration in 2% aqueous KCl solution were prepared. The densities of the solutions were measured by specific gravity bottle by relative measurement method with an accuracy of ±0.1 $kg.m^{-3}$at constant temperature using digital constant temperature water bath having an accuracy of ±0.1K. The viscosity measurements were done by using Ostwald's viscometer. The ultrasonic velocity of solvent and solution of different concentration at different temperature range (288.15 K to 303.15 K) were measured by using digital ultrasonic interferometer at frequency 2MHz (VI Microsystems Pvt. Ltd. Perungudi, Chennai) with an accuracy of ±0.1%.

PHYSICAL PARAMETERS

Following mathematical equations were used to calculate the derived parameters.

Adiabatic compressibility (β)

$$\beta = \frac{1}{\rho U^2}$$

Where ρ and U are the density and ultrasonic velocity of solution

Intermolecular free length (L_f)

$$L_f = K\beta^{1/2}$$

---------- (2)

Where, Kis Jacobson's constant.

This constant is a temperature dependent parameter whose value at any temperature (T) is given by (93.875+0.345T) $x10^{-8}$.

Acoustic impedance (Z)

$$Z = U\rho$$

Internal pressure (π_i)

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}}\right)^{7/6}$$

Where, b - stands for cubical packing, which is assumed to 2 for all the liquids

K- is a dimensionless constant independent of temperature

T- is the absolute temperature in Kelvin

M_{eff}- is the effective molecular weight

R- is gas constant

Relaxation time (τ)

$$\tau = \frac{4}{3}\eta\,\beta_a$$ ---------- (5)

Gibbs free energy (ΔG)

$$\Delta G = -K_B\,T\ln\left(\frac{h}{\tau K_B T}\right)$$---------- (6)

Where 'h' is Planck's constant and K_B- is Boltzmann constant = 1.3806 $x10^{-23}JK^{-1}$

---------- (1)

Rao's constant (R)

$$R = V_m U^{1/3}$$---------- (7)

Where, V_m is molar volume

Wada's constant (W)

$$W = \beta_a{}^{1/7} V_m$$ ---------- (8)

Molecular radius

$$r_o = (3M_{eff}/16\pi\rho V_m)^{1/3}[1 - (\gamma RgT/$$

$$MeffU2)\ MeffU23\gamma RgT + 1) - 11/3$$----------

(9)

RESULT AND DISCUSSION ---------- (3)

The experimentally measured valuesand derived thermo acousticparametersof solution of L-Valine in 2% aqueous solution of sodium chloride of different concentration (0.02 to 0.12) mol dm^{-3} at different temperature range T= (288.15, 293.15, 298.15 and 303.15) K are as given in Table1.

---------- (4)

Table 1. Measured parameters of L-Valine in 2 % aqueous KClof different concentrations at temperature range T= (288.15, 293.15, 298.15 and 303.15) K

Parameter	Tempt. K	Value of parameters measured for concentrations (mol.dm^{-3})					
		0.02	0.04	0.06	0.08	0.10	0.12
ρ (Kg m^{-3})	303.15 K	1001.73	1002.01	1002.09	1002.63	1003.18	1003.13
	298.15 K	1002.94	1003.61	1003.53	1004.31	1004.59	1005.07
	293.15 K	1003.77	1003.95	1004.2	1004.59	1005.22	1005.28
	288.15 K	1004.69	1005.13	1005.5	1006.26	1006.58	1006.64
η 10^{-3} (Nsm^{-2})	303.15 K	0.8209	0.8211	0.8306	0.8405	0.841	0.8504
	298.15 K	0.9044	0.9148	0.9147	0.9251	0.9351	0.9356
	293.15 K	0.9973	1.0077	1.0079	1.0185	1.0293	1.0498
	288.15 K	1.1548	1.1663	1.1667	1.1786	1.19	1.179
U (ms^{-1})	303.15 K	1515.936	1518.044	1520.862	1522.983	1524.401	1525.821
	298.15 K	1492.456	1494.499	1511.739	1515.235	1515.235	1518.747

	293.15 K	1499.286	1500.66	1502.725	1506.179	1507.565	1510.45
	288.15 K	1487.712	1490.113	1493.136	1495.181	1497.915	1500.66
βa $10^{-10}(m^2N^{-1})$	303.15 K	4.344	4.3307	4.3144	4.3	4.2896	4.2819
	298.15 K	4.4763	4.4611	4.3603	4.3368	4.3356	4.3136
	293.15 K	4.432	4.4231	4.4098	4.3879	4.3771	4.3601
	288.15 K	4.4971	4.4806	4.4609	4.4453	4.4277	4.4113
L_f 10^{-11}(m)	303.15 K	4.1353	4.129	4.1212	4.1143	4.1094	4.1057
	298.15 K	4.1612	4.1542	4.107	4.0959	4.0953	4.0849
	293.15 K	4.1031	4.099	4.0928	4.0826	4.0776	4.0697
	288.15 K	4.0977	4.0902	4.0812	4.0741	4.066	4.0584
Z $10^6(Kgm^2s^{-1})$	303.15 K	1.5186	1.5211	1.524	1.527	1.5293	1.5306
	298.15 K	1.4968	1.4999	1.5171	1.5218	1.5222	1.5264
	293.15 K	1.5049	1.5066	1.509	1.5131	1.5154	1.5184
	288.15 K	1.4947	1.4978	1.5014	1.5045	1.5078	1.5106
πi 10^9 (Nm^{-2})	303.15 K	2.574	2.5672	2.574	2.5827	2.5774	2.5847
	298.15 K	2.6802	2.6888	2.6672	2.6747	2.6836	2.6761
	293.15 K	2.7625	2.7696	2.7623	2.7682	2.7765	2.7952
	288.15 K	2.9349	2.9414	2.9332	2.941	2.9465	2.9239
τ 10^{-13} (s)	303.15 K	4.7545	4.7413	4.7781	4.8189	4.8099	4.8549
	298.15 K	5.398	5.4412	5.3178	5.3496	5.4059	5.3809
	293.15 K	5.8935	5.9427	5.9264	5.9588	6.0074	6.1029
	288.15 K	6.9241	6.9675	6.9393	6.9856	7.0252	6.9347
ΔG 10^{-21} $(kJmol^{-1})$	303.15 K	4.6069	4.5952	4.6276	4.6632	4.6554	4.6944
	298.15 K	4.9851	5.0179	4.9234	4.948	4.9911	4.972
	293.15 K	5.1885	5.2222	5.2111	5.2332	5.266	5.3299
	288.15 K	5.6729	5.6977	5.6816	5.7081	5.7306	5.679

R $10^{-4}(m^3mol^{-1})$	303.15 K	1.8353	1.8385	1.842	1.8448	1.8477	1.8512
	298.15 K	1.8339	1.8366	1.8402	1.8428	1.8459	1.8489
	293.15 K	1.8329	1.8362	1.8394	1.8424	1.8452	1.8486
	288.15 K	1.8317	1.8347	1.8378	1.8404	1.8435	1.8469
W $10^{-4}(m^3mol^{-1})$	303.15 K	3.9894	3.9978	4.0073	4.0147	4.0215	4.0304
	298.15 K	3.9676	3.9745	3.9955	4.0031	4.0097	4.0184
	293.15 K	3.9699	3.978	3.9863	3.9953	4.0018	4.0114
	288.15 K	3.9581	3.966	3.9747	3.9812	3.9898	3.9993
ro $10^{-4}(m^3mol^{-1})$	303.15 K	1.3887	1.3911	1.3939	1.3962	1.3982	1.4004
	298.15 K	1.383	1.3852	1.3949	1.3977	1.3991	1.4021
	293.15 K	1.3918	1.3939	1.3963	1.3993	1.4012	1.4041
	288.15 K	1.3919	1.3944	1.3972	1.3994	1.4021	1.4049

From table 1, it is observed that density of L-Valine solution in 2 % aqueous KCl increases with increase in concentration of solution due to increase in mass of the solution [6]. It decreases with temperature as volume of the solution increases with the rise in temperature. It is observed from table 1,that viscosity of L-Valine solution increases with increase in concentration.Increase in viscosity of solution with concentration suggests the strong interaction of solute and solvent molecule. Decreases in viscosity with rise in temperature can be explained as: with the rise in temperature molecules in the solution acquires more and more thermal energy. The motion of molecules increases at the expense of cohesive forces acting between the molecules. Since the solution faces lesser resistance to flow, the viscosity of the solution will decrease [7].

The increase in ultrasonic velocity with concentration (table 1) in any solution indicates the presence of solute-solvent interactions [8]. The increase in ultrasonic velocity with rise in concentration for the present system confirms the greater molecular association. As temperature increases, breaking of hydrogen bonding increases. This results in more and more number of monomeric water molecules. These molecules then enter in the cage-like water structure and get trapped to form closed packed structure. This closed-packed structure forms stiff material medium for the propagation of ultrasonic wave. Hence ultrasonic velocity increases with the rise in temperature.

The decrease in adiabatic compressibility values with concentration indicate that the hydrogen bonding between the unlike components in the solution decreases [9]. Adiabatic compressibility is inversely correlated with ultrasonic velocity which increases with increase in temperature. Hence adiabatic compressibility values decreases with increase in temperature.

The decrease in free length (table 1) with rise in concentration of L-Valine solution in 2% aqueous electrolytic solution suggest that there is a significant interaction between solute and solvent molecules. It also suggests the structure promoting behavior [10] as well as the presence of dipole-dipole and acceptor-donor interaction between solute and solvent molecules. The higher values of free length for higher temperature are due to more spacing among the components of the medium.

Acoustic impedance depends on the density of the medium and the speed of the

sound wave. Table 1, shows the variation of acoustic impedance with concentration and temperature. The increase in acoustic impedance with the increase in concentration as well as temperature suggests the greater association of solute and solvent through hydrogen bonding. Thus increase in acoustic impedance indicates associative nature of solute and solvent and enhancement in molecular interaction.

The internal pressure is the cohesive force or binding force, which is a resultant force of attraction and repulsion between the molecules. From table 1, it is observed that decrease in internal pressure with increase in temperature is due to the thermal agitation of molecules which reduces the interaction between the molecules in the system.

The intermolecular interactions can also be detected from physical parameter relaxation time and Gibbs' free energy. It is observed from table 1, that both the parameters increase slowly with increase in concentration but decreases with increase in temperature. This suggests greater association among components of the solution through intermolecular hydrogen bonding.

The increasing trend of Rao's constant and Wada's constant with rise in concentration as well as with temperature suggests greater molecular association and close packing of the medium.The increase in molecular radius values indicates greater association among the components of the mixture and enhanced solute solvent interactions.

CONCLUSIONS

Ultrasonic and viscometric measurements were carried on L-Valine solution in 2% aqueous KCl of different concentration at different temperatures. It is concluded that strength of intermolecular interaction increases with increase inconcentration of L-Valine which indicates solute-solvent interactions.

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