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Study of Interactions of Tryptophan through Acoustic and Thermodynamic Properties

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Abstract

Molecular interactions of Tryptophan (an essential amino acid) in the presence of essential metal ions like Zn^{2+} and Co^{2+} at 303.15K have been studied by using ultrasonic interferometer supplied by M/s Mittal Enterprises, New Delhi, operating at a frequency of 2 MHz. and a bicapillary pyknometer to measure the density of solution. The data is processed to obtain the various acoustic and thermodynamic parameters to study the molecular interactions in aqueous solutions. The values of apparent molar volume, apparent molar compressibility, partial molar volume, partial molar compressibility, specific acoustic impedance, relative association, intermolecular free length have been calculated by using standard mathematical relations. The concentration dependences of the density and ultrasonic velocity were tried to fit into linear and polynomial equations. It is interesting to see the associative interaction among the molecules and ions as well as the increase in the stacking interactions between the metal ions and tryptophan.

Keywords: Interactions, biomolecules, ultrasonic, molar volume, compressibility.

Introduction

The study of biomolecular interactions have been of intense activity in the recent past in all branches of chemistry and in other parallel disciplines as well, since these interactions are the driving force for the essential biochemical reactions. Amino acids, nucleosides and nucleotides are the important biochemicals in life processes, as these constitute a part of proteins, nucleic acids and other essential biomolecules. Also the metals like iron, zinc, cobalt, magnesium etc have been recognized as essential micronutrients, which provide structure and activity basis to several metallobiomolecular systems. Investigation of conformational properties of such biomolecules, interactions of their chemical groups with metal ions and their interaction in aqueous solution play an important role in understanding the biochemical processes occurring in the living systems.

Material and Methods

Tryptophans (AR grade, Qualigens fine chemicals Pvt. Ltd., Bombay, India) were used without further purification. The solutions were prepared by using triple distilled water. The purity of triple distilled water was further ascertained by measuring it's ultrasonic velocity at 298.15K, which agreed with the corresponding literature values[1]. The ultrasonic interferometer and bycapilliary pyknometer was calibrated before the measurements. The aqueous solutions of various concentrations of tryptophan with $CaCl_2$ as well as with $CoCl_2$ were prepared by using triple distilled water.

Data Analysis: The experimentally calculated values of density, ultrasonic velocity, relative viscosity, apparent molar volume and apparent molar compressibility, for tryptophan in aqueous solution of Zn^{2+} and Co^{2+} at 303.15K, are recorded in table 1 and 2.

The values of partial molar volume and partial molar compressibility are calculated by using following equations.

$$\phi_v = \phi^0_v + S_v m \quad (1)$$

$$\phi_k = \phi^0_k + S_k m \quad (2)$$

Where, ϕ^0_v and ϕ^0_k are apparent molar volume and compressibility respectively at infinite dilution and S_v and S_k are experimental slopes. These limiting values of apparent molar volumes and compressibility along with the slopes are listed in the table 5.

The concentration dependence of ultrasonic velocity of sound and density were tried to fit into following equations.

$$Y = a_y + b_y m. \quad (3)$$

$$Y = a_y + b_y m + c_y m^2 \quad (4)$$

Where $Y = u$ or ρ and $a_y = u_0$ or ρ_0 .

u_0 is the velocity of sound in pure solvent and ρ_0 is density of pure solvent. The equation (D) yields better fit than the equation (C).

The table 1 and 2 indicates that the values of density, ultrasonic velocity and relative viscosity increase with increase in the concentration of tryptophan in aqueous solutions of Zn^{2+} and Co^{2+}. These values are higher for 0.05 M Zn^{2+} solutions and decrease continuously with the decrease in concentration Zn^{2+}. This may be attributed to the cohesion brought about by ionic hydration[2]. A similar trend of variation is also observed for tryptophan in 0.05M, 0.01M, and 0.005 M Co^{2+} solution. The values of density, ultrasonic velocity and relative viscosities are higher for tryptophan in Co^{2+} solution than in Zn^{2+} solution. This may indicate stronger interaction of tryptophan in aqueous solution of Co^{2+}.

Table-1
Density, relative viscosity, ultrasonic velocity, apparent molar volume apparent molar compressibility of tryptophan in 0.05, 0.01 and 0.005M Zinc Chloride solution at 303.15K

Molality	Density	Relative Viscosity	Ultrasonic Velocity	Apparent molar Volume	Apparent Molar Compressiblity
m	ρx10^{-3}	η_r	U	ϕ_v x10^{-6}	ϕ_kx10^{-15}
(moles.kg^{-1})	*(Kg.cm^{-3})*		*(ms^{-1})*	*(m^{3}mol^{-1})*	*(m^{3}mol^{-1}pa)*
0.05M zinc chloride					
0.005016	1.002062	1.0079	1502.98	162.304	-1.5117
0.010004	1.002262	1.0162	1503.39	163.052	-4.2982
0.015087	1.002461	1.0237	1503.89	163.603	-3.555
0.020212	1.002658	1.0298	1504.48	164.039	-5.5272
0.025024	1.002823	1.0341	1504.91	165.073	-3.0478
0.03011	1.002998	1.0399	1505.57	165.776	-5.3038
0.01M zinc chloride					
0.005037	0.997262	1.0035	1499.78	139.692	-3.6486
0.01008	0.997586	1.0151	1500.38	139.885	-3.7035
0.015131	0.997899	1.0202	1500.78	140.687	-2.8592
0.020189	0.998212	1.0286	1501.17	141.085	-2.4048
0.025116	0.998498	1.0321	1501.77	142.06	-2.5936
0.030198	0.998809	1.0389	1502.17	142.184	-2.3389
0.005M zinc chloride					
0.005073	0.996661	1.0024	1498.79	145.563	-3.1508
0.010154	0.996958	1.0103	1499.19	145.762	-1.9974
0.015083	0.997246	1.0138	1499.59	145.807	-1.6685
0.020178	0.997537	1.0206	1499.98	146.146	-1.398
0.025122	0.997821	1.0273	1500.58	146.259	-1.7755
0.030232	0.998114	1.0308	1501.18	146.343	-1.9936

Table-2
Density, relative viscosity, ultrasonic velocity, apparent molar volume apparent molar compressibility of tryptophan in 0.05, 0.01 and 0.005M CobaltousChloride solution at 303.15K

Molality	Density	Relative Viscosity	Ultrasonic Velocity	Apparent molar Volume	Apparent Molar Compressiblity
m	**ρx10^{-3}**	**η_r**	**u**	**ϕ_v x10^{-6}**	**ϕ_kx10^{-15}**
(moles.kg^{-1})	***(Kg.cm^{-3})***		***(ms^{-1})***	***(m^{3}mol^{-1})***	***(m^{3}mol^{-1}pa)***
0.05M cobaltous chloride					
0.005126	1.00226	1.0081	1503.56	149.375	3.066
0.010094	1.002528	1.0169	1504.16	149.671	-1.5381
0.01507	1.002792	1.0248	1504.76	150.037	-1.9283
0.020054	1.003059	1.0302	1505.55	150.072	-2.6861
0.025043	1.003323	1.0356	1506.14	150.208	-2.6628
0.030209	1.003594	1.0412	1506.94	150.368	-3.0037
0.01M cobaltous chloride					
0.005072	0.997341	1.0042	1501.38	147.471	-7.6596
0.010151	0.997626	1.0133	1501.77	147.868	-6.3262
0.015079	0.997899	1.0199	1502.17	148.204	-6.5467
0.020172	0.998182	1.0266	1502.76	148.317	-1.1913
0.025115	0.998453	1.0332	1503.36	148.511	-1.5559
0.030223	0.998769	1.0367	1503.77	147.433	-1.5002
0.005M cobaltous chloride					
0.00505	0.9967883	1.0035	1500.38	150.609	-2.521
0.010121	0.997048	1.0101	1500.78	151.929	-2.2474
0.015091	0.997298	1.0167	1501.18	152.642	-2.2083
0.019867	0.997522	1.0201	1501.57	153.798	-1.6325
0.025111	0.997739	1.0267	1502.17	155.707	-4.3161
0.030744	0.997999	1.0334	1502.56	156.137	-2.0225

Table-3
Specific acoustic impedence,relative association,isentropic compressibility, intermolecular free-length and conductance of tryptophan in 0.05, 0.01 and 0.005M Zinc Chloride solution at 303.15K

Molality	Specific acou. Impedence	Relative Association	Isentropic Compress.	free length	Conductance
m	Z x10^{-3}	R_A	Ks	L_f	λ x10^{-3}
(moles.kg^{-1})	*(Kg.m^{-2} s^{-1})*			*A^0*	*mhos.cm^{-2}*
0.05M zinc chloride					
0.005016	1506.079	1.000078	4.4177	0.40003	7.14
0.010004	1506.791	1.000186	4.4144	0.39988	7.08
0.015087	1507.591	1.000274	4.4106	0.39971	6.98
0.020212	1508.479	1.00034	4.4063	0.39951	6.87
0.025024	1509.158	1.000409	4.4031	0.39937	6.76
0.03011	1510.084	1.000438	4.3984	0.39916	6.63
0.01M zinc chloride					
0.005037	1495.674	1.000196	4.458	0.40185	1.81
0.01008	1496.758	1.000387	4.4529	0.40162	1.8
0.015131	1497.627	1.000612	4.4492	0.40145	1.79
0.020189	1498.486	1.00084	4.4455	0.40129	1.78
0.025116	1499.514	1.000993	4.4406	0.40107	1.77
0.030198	1500.381	1.001216	4.4369	0.4009	1.75
0.005M zinc chloride					
0.005073	1493.786	1.000169	4.4665	0.40224	0.949
0.010154	1494.629	1.000378	4.4628	0.40207	0.947
0.015083	1495.46	1.000578	4.4592	0.4019	0.944
0.020178	1496.286	1.000783	4.4555	0.40174	0.942
0.025122	1497.31	1.000935	4.4507	0.40152	0.94
0.030232	1498.349	1.001095	4.4458	0.4013	0.935

Table-4
Specific acoustic impedence,relative association, isentropic compressibility, intermolecular free-length and conductance of tryptophan in 0.05, 0.01 and 0.005M Zinc Chloride solution at 303.15K

Molality	Specific acou. Impedence	Relative Association	Isentropic Compress.	Intermolecular free length	Conducta nce
m	Z x10^{-3}	R_A	Ks	L_f	λ x10^{-3}
(moles.kg^{-1})	*(Kg.m^{-2} s^{-1})*			*A^0*	*mhos.cm^{-2}*
0.05M Cobaltous chloride					
0.005126	1506.958	1.000191	4.4134	0.39984	7.15
0.010094	1507.963	1.000325	4.4087	0.39963	7.08
0.01507	1508.961	1.000456	4.4041	0.39941	6.99
0.020054	1510.155	1.000547	4.3983	0.39915	6.95
0.025043	1511.145	1.00068	4.3937	0.39894	6.89
0.030209	1512.356	1.000773	4.3878	0.39868	6.76
0.01M Cobaltous chloride					
0.005072	1497.388	1.000201	4.4481	0.40141	1.898
0.010151	1498.205	1.0004	4.4445	0.40124	1.896
0.015079	1499.014	1.000585	4.4409	0.40108	1.89
0.020172	1500.028	1.000738	4.4362	0.40087	1.882
0.025115	1501.034	1.000876	4.4315	0.40065	1.867
0.030223	1501.919	1.001102	4.4276	0.40048	1.856
0.005M Cobaltous chloride					
0.00505	1495.561	1.000187	4.4565	0.40178	1.039
0.010121	1496.35	1.000358	4.453	0.40162	1.031
0.015091	1497.124	1.00052	4.4495	0.40147	1.027
0.019867	1497.849	1.000658	4.4462	0.40132	1.023
0.025111	1498.774	1.000743	4.4417	0.40111	1.017
0.030744	1499.553	1.000917	4.4382	0.40096	1.004

Table-5
Limiting values of apparent molar volume and apparent molar compressibility for tryptophan along with slops at 303.15 K

Conc. of Zinc Chloride	$\phi^0_v \times 10^{-6}$ (m^3mol^{-1})	$\phi^0_k \times 10^{-15}$ ($m^3mol^{-1}pa^{-1}$)	$S_v \times 10^{-6}$ ($m^3mol^{-2}kg$)	$S_k \times 10^{-15}$ ($m^3mol^{-2}pa^{-1}kg$)
0.05 M	161.59	-9.02	135.71	0.0002
0.01 M	138.99	-4.12	110.11	0.0005
0.005 M	145.41	-3.42	32.597	0.0011

Results and Discussion

Volumetric data: From the table 1 and 2, it is evident that the values of apparent molar volume (ϕ_v) are positive and increase gradually with increase in concentration of tryptophan in 0.05M, 0.01M and 0.005 M aqueous solution of Zn^{2+} and Co^{2+}. This clearly indicates that there are strong solute-solvent, solvent-solvent and ion-solvent interactions. The ϕ_v values decrease with decrease in the concentration of metal ions, which may be attributed to the ionic concentration and electrostriction effect[3]. This may be accounted to the associative interaction among the molecules and ions also increase the stacking interactions between the metal ions and tryptophan. Several workers[4-7] have also reported the volumetric studies of different amino acids in aqueous solution of electrolytes.

The plots of ϕ_v versus m show that the ϕ_v for tryptophan is linear function of its molal concentration (m). The slopes of plots of ϕ_v versus m are positive for all concentration of Zn^{2+} and Co^{2+}. The graphically calculated values of ϕ^0_v along with slopes are listed in the table 5. The data of table 5 shows that the ϕ^0_v values are positive and higher for tryptophan at experimental temperature, indicating strong solute-solvent and ion-solvent interactions, at infinite dilution. Since tryptophan is an amino acid with non-polar R-group, it is less interactive towards the water molecules. But the presence of metal cations enhances the possibility of strong interaction through complexation. This fact is further supported by positive values of S_v for tryptophan in Zn^{2+} and Co^{2+} solutions.

Compressibility data: Table 1, 2 and 7 shows the variation in compressibility in terms of ϕ_k and ϕ^o_K values for tryptophan in Zn^{2+} and Co^{2+} solutions. The negative ϕ_k values indicate the loss of structural compressibility of solvent molecules and these solutions are incompressible due to complex formation between tryptophan and Zn^{2+} or Co^{2+}. These complex molecules may occupy interstitial space in a network structure associated with tetrahedrally bonded water molecules.

The ϕ_k values are found to increase with concentration of tryptophan in aqueous solutions of Zn^{2+} whereas in Co^{2+} solutions the reverse trend is observed except for 0.005M solutions where the variation gives nearly flat line. According to hypothesis of substitutional dissolution, the complex molecule and the free tryptophan molecule can be thought of as occupying the cavities exists in open water structure. Such suitable cavities are created according to the shape and size of solutes leading to strengthening of water structure in the vicinity of solute molecule giving negative value of ϕ_k. The difference in the variation of ϕ_k with concentration of tryptophan in Zn^{2+} and Co^{2+} solution may be due to difference in the size of respective metal ion as well as the suitability of the cavities in water structure for their fitting.

The concentration dependence of apparent molar compressibility (ϕ_k) has been used to obtain the limiting molar compressibility (ϕ^0_k) values. The partial molar compressibility values for tryptophan in Zn^{2+} and Co^{2+} solutions are listed in the table 5. The values are more negative than those reported for amino acid in water[8,9]. The decrease in isentropic compressibility (K_s) with increase in concentration of tryptophan in aqueous solution of Zn^{2+} and Co^{2+} (table 3 and 4) may be due to approach of solvent molecules[10] around the metal ions supporting the strong ion-solvent interaction. This may also support the formation of week H-boding between oxygen atom of water molecule and H-atom of COOH group of tryptophan molecule. Since tryptophan is an amino acid with non-polar R-group, it is less interactive towards the water molecules. But the presence of metal cations enhances the possibility of strong interactions through complexation.

The parameter Z (acoustic impedance) shows linear variation with concentration of tryptophan (table 3, 4). The Z values decrease with decrease in concentration of metal ion. This may also be correlated with size of metal ions.

In the present study relative association (R_A) increases with concentration suggesting that the solute-solvent interaction dominates.

Viscosity Data: The values of relative viscosity of tryptophan in 0.05 M, 0.01M and 0.005 M aqueous solution of Zn^{2+} and Co^{2+} at 303.15K are given in the table 1 and 2 It can be observed from the table that the relative viscosity of tryptophan increases with increase in concentration of tryptophan as well as the concentration of aqueous solution of Zn^{2+} and Co^{2+}.

Conclusion

The overall data analysis for tryptophan in aqueous solution of Zn^{2+} and Co^{2+} suggest that in these solutions, complex formation occurs and fitting of such complexes at interstitial site of water network is more probable. It also indicates the loss of compressibility of solvent due to strong electrostrictive forces in the vicinity of ions, causing electrostictive solvation of ions.

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