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INTERACTIONS OF L-PROLINE IN AQUEOUS K_2SO_4, KNO_3 AND KCl AT TEMPERATURES 303.15, 308.15, 313.15, 318.15 AND 323.15 K

RIFFAT BASHARAT*

Department of Chemistry, Govt. Degree College, SOPORE (J & K) INDIA

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ABSTRACT

Density and ultrasonic velocity of L-proline have been carried out in K_2SO_4 + water, KNO_3 + water and KCl + water at different temperatures, 303.15, 308.15, 313.15, 318.15 and 323.15 K. The thermodynamic parameters such as apparent molal volume and apparent molal isentropic compressibility have been calculated. The values of these parameters have been further used to derive the apparent molal volume at infinite dilution i.e. partial molal volume, (ϕ_v^0) and apparent molal isentropic compressibility at infinite dilution i.e partial molal compressibility, (ϕ_k^0) for L-proline in the said aqueous solution of electrolytes. The results were discussed in terms of solute- solute and solute- solvent interactions.

Key words: Ultrasonic velocity, Density, L-proline, Electrolytes.

INTRODUCTION

The study of ultrasonic velocity and density of amino acids in aqueous electrolyte solutions provide a better understanding of the nature of interactions between the solute and solvent. It can also provide useful information regarding conformational stability and interactions in ternary systems, for theoretical applications and for practical purposes. The addition of salt enhances the structural modifications in amino acid mixtures and also influences their properties[1-3]. Electrolytes are known to influence the stability of biologically important molecules such as proteins. Since proteins are complex molecules and their behavior in solutions is governed by a combination of many more specific interactions, direct study of electrolyte-protein is difficult. Since amino acids serve as building blocks of proteins, so it is important to study the thermodynamic properties of amino acids in presence of electrolytes. Thermodynamic properties of amino acids in aqueous electrolyte solutions provide important information about solute-solvent and solute-solute interactions that can be of great help in understanding the effect of electrolytes on biologically important systems[4-7]. The investigation of volumetric and thermodynamic properties of amino acids and peptides in aqueous and mixed aqueous solvents has been the area of interest of a number of researchers[8-12]. In the present paper, ultrasonic velocity and density studies were carried out in aqueous solutions of L-proline in presence of electrolytes and the data is further used to calculate the important thermodynamic parameters i.e. apparent molal volume/partial molal volume, apparent molal isentropic compressibility/partial molal compressibility.

Available online at www.sadgurupublications.com
*Author for correspondence; E-mail: riffat_ehtisham@rediffmail.com

EXPERIMENTAL

The amino acid: L-proline and the electrolytes : K_2SO_4, KNO_3 and KCl (≥ 99% purity) were purchased from SRL (India) and E. Merck (India). The amino acid was dried at ~110°C and the salts were re-crystallized twice in triply distilled water before use. The ultrasonic velocity was measured with ultrasonic interferometer (Mittals Model : M-77 India) at 4 MHz and was based on variable path - principle. An average of 10 readings was taken as a final value of ultrasonic velocity. The densities of solutions were measured by pyknometer. Thermostated paraffin/water bath was maintained at a desired temperature (± 0.01°) for about 30 minutes prior to recording of readings. The uncertainty of density measurements was up to ± 0.0002 g/cm^3 and of ultrasonic velocity was ± 0.2 m/s. The density and ultrasonic parameters such as partial molal volume and partial molal isentropic compressibility were computed at different temperatures and concentrations.

RESULTS AND DISCUSSION

The values of apparent molar volume ϕ_v were calculated from the measured densities using the following equation:

$$\phi_v = (M/\rho) - \{1000\,(\rho - \rho_o)/m\rho\rho_o$$

where M is the molar mass of the solute, m is the molality of the amino acid in electrolyte-water mixtures, ρ and ρ_o are the densities of the amino acid–salt–water ternary system and solvent, respectively. The results of the density measurements from 303.15 K to 323.15 K are given in Table 1 and that of apparent molal volumes are presented in Table 1(a).

Table 1: Density values ($\rho/10^3$ Kg m^{-3}) as functions of concentration and temperature

(i) L-proline in aqueous K_2SO_4 solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	308.15	313.15	318.15	323.15
0.0000	1.0593	1.0579	1.0561	1.0542	1.0519
0.0953	1.0606	1.0592	1.0576	1.0557	1.0534
0.2909	1.0658	1.0643	1.0626	1.0606	1.0584
0.4934	1.0709	1.0694	1.0677	1.0656	1.0633
0.7032	1.0760	1.0745	1.0727	1.0706	1.0683
0.9206	1.0812	1.0796	1.0777	1.0756	1.0733
1.1462	1.0863	1.0847	1.0827	1.0806	1.0782

(ii) L- proline in aqueous KNO_3 solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	308.15	313.15	318.15	323.15
0.0000	1.0529	1.0511	1.0490	1.0467	1.0442
0.0958	1.0554	1.0535	1.0514	1.0491	1.0466
0.1932	1.0580	1.0561	1.0539	1.0516	1.0492

Cont…

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	308.15	313.15	318.15	323.15
0.2923	1.0608	1.0588	1.0566	1.0542	1.0516
0.3932	1.0634	1.0614	1.0592	1.0568	1.0542
0.4958	1.0661	1.0640	1.0618	1.0593	1.0568
0.6002	1.0688	1.0667	1.0645	1.0619	1.0592
0.7065	1.0714	1.0692	1.0670	1.0645	1.0618
0.8146	1.0742	1.0719	1.0697	1.0670	1.0643
0.9248	1.0768	1.0744	1.0724	1.0696	1.0669
1.0371	1.0794	1.0771	1.0749	1.0721	1.0694

(iii) L-proline in aqueous KCl solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	308.15	313.15	318.15	323.15
0.0000	1.0614	1.0597	1.0578	1.0556	1.0533
0.0950	1.0630	1.0614	1.0595	1.0573	1.0549
0.2900	1.0677	1.0660	1.0641	1.0618	1.0594
0.4920	1.0724	1.0706	1.0686	1.0664	1.0639
0.7015	1.0770	1.0752	1.0732	1.0709	1.0684
0.9189	1.0817	1.0799	1.0778	1.0755	1.0729
1.1445	1.0863	1.0845	1.0824	1.0800	1.0774

Table 1(a): Apparent molal volume (ϕ_v x 10^6, m^3 mol^{-1}) as functions of concentration and temperature

(i) L-proline in aqueous K_2SO_4 solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	308.15	313.15	318.15	323.15
0.0953	96.41	96.52	94.77	94.92	95.09
0.2909	88.23	88.63	88.44	88.88	88.71
0.4934	86.78	87.06	86.98	87.48	87.62
0.7032	86.16	86.38	86.49	86.87	87.02
0.9206	85.71	86.00	86.22	86.53	86.68
1.1462	85.51	85.76	86.04	86.32	86.55

(ii) L-proline in aqueous KNO_3 solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	308.15	313.15	318.15	323.15
0.0958	85.60	86.66	86.79	86.93	87.08
0.1932	85.13	85.71	86.31	86.44	86.11
0.2923	84.34	85.07	85.51	85.96	86.43
0.3932	84.41	84.99	85.35	85.72	86.11

Cont…

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.4958	84.27	84.94	85.25	85.76	85.91
0.6002	84.19	84.75	85.03	85.63	86.10
0.7065	84.24	84.88	85.14	85.54	85.96
0.8146	84.06	84.75	84.98	85.59	85.97
0.9248	84.12	84.85	84.86	85.52	85.88
1.0371	84.18	84.74	84.96	85.56	85.90

(iii) L-proline in aqueous KCl solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0950	93.38	92.56	92.69	92.85	93.98
0.2900	88.66	88.77	88.89	89.35	89.82
0.4920	87.72	88.01	88.32	88.46	88.99
0.7015	87.44	87.68	87.94	88.21	88.63
0.9189	87.19	87.40	87.73	87.97	88.43
1.1445	87.11	87.30	87.59	87.90	88.30

An examination of the above table reveals that the partial molal volume of the said amino acid in aqueous electrolyte solutions at each temperature are higher than the corresponding values in aqueous medium. The calculated apparent molal volume data is correlated using the following linear function:

$$\phi_v = \phi_v^0 + S_v m$$

The parameter S_v is the volumetric virial coefficient. The values of the partial molal volume or the infinite dilution apparent molal volume along with those of S_v are given in Table 1(b):

Table 1(b): The infinite dilution apparent molal volume at different temperatures

(i) L-proline in aqueous K_2SO_4 solution

Temperature (K)	ϕ_v^0 x 10^6 (m^3 mol^{-1})	S_v x 10^6 (m^3 mol^{-2} Kg)	σ x 10^6 (m^3 mol^{-1})
303.15	88.63	-3.021	0.5
308.15	89.01	-3.155	0.5
313.15	88.67	-2.576	0.5
318.15	89.22	-2.816	0.5
323.15	89.05	-2.441	0.4

Cont…

(ii) L-proline in aqueous KNO_3 solution

Temperature (K)	ϕ_v^0 x 10^6 (m^3 mol^{-1})	S_v x 10^6 (m^3 mol^{-2} Kg)	σ x 10^6 (m^3 mol^{-1})
303.15	85.15	-1.248	0.3
308.15	85.94	-1.453	0.4
313.15	86.38	-1.726	0.4
318.15	86.54	-1.218	0.3
323.15	86.62	-0.847	0.3

(iii) L-proline in aqueous KCl solution

Temperature (K)	ϕ_v^0 x 10^6 (m^3 mol^{-1})	S_v x 10^6 (m^3 mol^{-2} kg)	σ x 10^6 (m^3 mol^{-1})
303.15	88.82	-1.684	0.3
308.15	89.00	-1.650	0.2
313.15	89.15	-1.484	0.2
318.15	89.49	-1.572	0.3
323.15	90.02	-1.671	0.3

It is noteworthy that the ϕ_v^0 values in case of L-proline in the said three electrolytes have been found to be 89.20, 83.52 and 89.07 cm^3/mol, respectively at 298.15 K, while in aqueous medium it is found to be 82.83 cm^3/mol[13]. The sign of S_v is determined by the nature of the interaction between the solute species. For zwitter-ionic amino acid, the positive values of S_v suggest that the pairwise interaction is dominated by the interaction of the charged functional groups. The values of ϕ_v^0 are positive for all the systems of L-proline in aqueous K_2SO_4, KNO_3 and KCl solutions. These positive values of ϕ_v^0 indicate relatively stronger solute-solvent interactions. These values also show an increasing trend with an increase in the temperature. The increase in ϕ_v^0 values with temperature may be attributed to volume expansion of hydrated zwitter-ions of amino acid.

The ultrasonic velocity data is given in the table mentioned as number 2. The experimental data for L-proline in 0.5 M K_2SO_4, 1 M KNO_3 and 1.5 M KCl aqueous mixtures were obtained at different amino acid concentrations, in the range domain of temperatures between 303.15 K to 323.15 K.

Table 2: Ultrasonic velocity values (u/m. s^{-1}) as functions of concentration and temperature

(i) L-proline in aqueous K_2SO_4 solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	1571.2	1578.8	1587.6	1592.6	1597.6
0.0953	1577.2	1585.2	1592.4	1597.2	1601.6
0.2909	1589.2	1596.4	1604.4	1608.6	1612.8
0.4934	1604.2	1611.4	1618.0	1622.4	1625.6
0.7032	1616.0	1621.4	1625.8	1630.4	1635.8
0.9206	1627.2	1631.2	1634.8	1640.2	1644.9
1.1462	1640.4	1644.4	1648.2	1651.8	1656.8

Cont…

(ii) L-proline in aqueous KNO_3 solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	1541.8	1550.2	1557.4	1563.6	1568.4
0.0958	1549.0	1552.4	1559.2	1564.8	1569.8
0.1932	1553.6	1558.1	1563.2	1568.6	1573.4
0.2923	1558.8	1563.9	1570.6	1575.2	1580.4
0.3932	1561.8	1567.2	1573.8	1581.4	1584.8
0.4958	1568.2	1575.4	1580.2	1585.6	1589.8
0.6002	1577.2	1581.2	1588.0	1594.4	1597.0
0.7065	1581.6	1585.6	1593.8	1599.0	1602.2
0.8146	1584.8	1591.2	1597.8	1602.4	1608.0
0.9248	1593.6	1600.8	1605.6	1609.6	1613.8
1.0371	1598.4	1604.4	1609.0	1612.0	1615.2

(iii) L-proline in aqueous KCl solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	1584.0	1590.4	1595.8	1601.6	1606.2
0.0950	1586.6	1593.6	1600.8	1607.0	1611.0
0.2900	1598.8	1606.8	1612.4	1617.2	1621.8
0.4920	1612.6	1617.8	1624.0	1627.6	1631.4
0.7015	1623.6	1630.8	1635.2	1638.8	1642.0
0.9189	1637.4	1641.3	1645.4	1649.2	1652.2
1.1445	1649.2	1654.4	1658.0	1660.7	1663.0

The ultrasonic velocity data is used to calculate the isentropic compressibility of different solutions by using the following relation:

$$\kappa_s = \frac{1}{\rho u^2}$$

The calculated values of isentropic compressibility were used to get the partial/apparent molal compressibility according to the given relation:

$$\phi_k = [\{1000\ (\kappa_s - \kappa_o)\}/m\rho_o] + \kappa_s\phi_v$$

where m is the molality, ρ_o is the density of the solvent and the respective values of κ_s and κ_o denote the isentropic compressibilities of solution and solvent. The sign $\phi_{v,}$ represent the partial/apparent molal volume.

The partial/apparent molal compressibility ϕ_k of amino acids in solutions with different concentrations are presented in Table 2a.

Table 2a: Apparent molal isentropic compressibility (ϕ_k x 10^{11}, $bar^{-1}m^3$ mol^{-1}) as functions of concentration and temperature

(i) L-proline in aqueous K_2SO_4 solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	308.15	313.15	318.15	323.15
0.0953	3.18	1.38	7.61	8.58	11.40
0.2909	-2.57	-1.59	-0.47	1.03	2.05
0.4934	-5.90	-5.25	-3.26	-2.39	-0.76
0.7032	-4.94	-3.32	-0.45	0.03	-0.18
0.9206	-3.99	-2.01	0.64	0.64	-0.81
1.1462	-3.94	-2.34	-0.22	0.46	0.56

(ii) L-proline in aqueous KNO_3 solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	308.15	313.15	318.15	323.15
0.0958	-4.69	14.06	16.02	18.96	17.94
0.1932	-5.70	4.58	10.20	12.17	11.78
0.2923	-4.90	1.68	2.29	5.17	4.77
0.3932	-1.30	2.84	3.79	2.31	4.19
0.4958	-2.57	-0.86	1.65	2.74	3.28
0.6002	-5.39	-1.41	-0.90	-0.64	1.34
0.7065	-4.07	-0.59	-1.08	-0.16	1.12
0.8146	-2.52	-0.81	-0.30	1.01	0.08
0.9248	-4.00	-2.81	-1.58	-0.04	0.04
1.0371	-3.29	-1.74	-0.43	1.39	2.27

(iii) L-proline in aqueous KCl solution

Concentration (mol Kg^{-1})	Temperature (K)				
	303.15	308.15	313.15	318.15	323.15
0.0950	17.11	13.55	0.52	3.41	6.89
0.2900	2.94	0.57	0.32	2.10	2.36
0.4920	-0.94	0.34	-0.18	1.80	2.80
0.7015	-0.45	-0.78	-0.01	0.15	2.55
0.9189	-1.40	-0.08	0.72	1.77	2.75
1.1445	-1.01	-0.43	0.41	1.72	2.77

The measured experimental data is correlated using the following linear function:

$$\phi_k = \phi_k^0 + S_k m$$

where ϕ_k^0 is infinite dilution apparent molal compressibility of the said solutions. S_k is the slope of the lines obtained from fitting the above equation to the experimental data. The values of the infinite dilution apparent molal compressibility of L-proline in K_2SO_4, KNO_3, and KCl solutions are presented in Table 2(b).

Table 2(b): The infinite dilution apparent molal isentropic compressibility at different temperatures

(i) L-proline in aqueous K_2SO_4 solution

Temperature (K)	ϕ_k^0 x 10^{11} (bar^{-1} m^3 mol^{-1})	S_k x 10^{11} (bar^{-1} m^3 mol^{-2} Kg)	σ x 10^{11} (bar^{-1} m^3 mol^{-1})
303.15	0.10	-0.51	0.3
308.15	-0.77	-0.23	0.2
313.15	3.27	-0.43	0.4
318.15	4.54	-0.52	0.4
323.15	7.06	-0.83	0.4

(ii) L-proline in aqueous KNO_3 solution

Temperature (K)	ϕ_k^0 x 10^{11} (bar^{-1} m^3 mol^{-1})	S_k x 10^{11} (bar^{-1} m^3 mol^{-2} Kg)	σ x 10^{11} (bar^{-1} m^3 mol^{-1})
303.15	-4.64	0.14	0.1
308.15	8.40	-1.24	0.3
313.15	11.24	-1.49	0.4
318.15	13.01	-1.57	0.4
323.15	12.86	-1.47	0.4

(iii) L-proline in aqueous KCl solution

Temperature (K)	ϕ_k^0 x 10^{11} (bar^{-1} m^3 mol^{-1})	S_k x 10^{11} (bar^{-1} m^3 mol^{-2} Kg)	σ x 10^{11} (bar^{-1} m^3 mol^{-1})
303.15	11.06	-1.38	0.5
308.15	8.09	-0.97	0.5
313.15	0.22	0.01	0.1
318.15	2.71	-0.15	0.1
323.15	4.94	-0.26	0.2

It has been observed that the apparent molal compressibility values for the said amino acid are negative in all the three systems. The S_k values were also found to be negative, which suggest the presence of essentially weak solute-solute interactions. The values show irregular trend of variations with temperature as well as with concentration. The negative ϕ_k values exhibit strong interactions between the solute and solvent. The ion-zwitterion interactions seem stronger than ion-hydrophobic interactions in systems under investigation. The ϕ_k^o values are positive of smaller magnitude. These values apparently indicate a larger ordering effect of the solute molecules on those of the solvent.

CONCLUSION

In the present study, the experimental data of density and ultrasonic velocity of L-proline in aqueous K_2SO_4, KNO_3 and KCl solutions at different temperatures and concentrations have been reported. From this data different parameters have been calculated which help to provide the better understanding of the significant interactions i.e ionic, dipolar and hydrophobic between amino acid and electrolytes.

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