Ultrasonic Velocities and Densities of L-Histidine or L-Glutamic Acid or L-Tryptophan or Glycylglycine + 2 $\text{mol}\cdot\text{L}^{-1}$ Aqueous KCl or KNO_3 Solutions from (298.15 to 323.15) K

Riyazuddeen* Tausif Altamash

Department of Chemistry, Aligarh Muslim University, Aligarh 202002, U.P., India

Ultrasonic velocity and density values of L-histidine or L-glutamic acid or L-tryptophan or glycylglycine + 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl or 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KNO_3 solution have been measured as functions of amino acid or dipeptide concentration and temperature from T = (298.15 to 323.15) K. Using ultrasonic velocity and density data, the thermodynamic parameters isentropic compressibility (κ_s) and change in isentropic compressibility values have been computed. The κ_s values decrease with an increase in the amino acid/dipeptide concentration as well as with temperature of the systems under investigation. The decrease in κ_s values with an increase in concentration of amino acid/dipeptide in aqueous solutions of KCl and KNO_3 has been ascribed to an increase in the number of incompressible zwitterions in the solutions.

Introduction

Measurements of ultrasonic velocity and density values of amino acids and peptides in aqueous electrolytes have been of interest with a view to improve the comprehension about the stability of native proteins and the equilibrium process between "folded" versus "unfolded" forms of proteins. As the amino acid and peptide molecules contain functional groups similar to those existing in the more complex proteins, they are expected to mimic some common features of proteins. A number of authors have measured the ultrasonic velocity and density values of amino acids and small peptides in aqueous electrolytic solutions.[1−17]

The present study is a continuation of our research program on the thermodynamic studies of amino acid−aqueous salt solution systems.[14−18] In this study, the ultrasonic velocity (u) and density (ρ) values of L-histidine or L-glutamic acid or L-tryptophan or glycylglycine + 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous solution of KCl or KNO_3 as functions of amino acid/peptide concentration and temperature [(298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K] have been reported. Using the u and ρ data, the isentropic compressibility (κ_s) and change in isentropic compressibility ($\Delta\kappa_s$) values have been evaluated with a view to investigating the zwitterions−ions, zwitterions−water dipoles, ions−water dipoles, and ions−ions interactions operative in the said systems.

Material and Methods

The amino acids and peptide (L-histidine, L-glutamic acid, L-tryptophan, and glycylglycine) and the salts [potassium chloride and potassium nitrate of high purity (≥ 99 %)] used in this study were purchased from SRL (India) and E. Merck (India), respectively. The amino acids were recrystalyzed twice in (ethanol + water) mixtures, dried at 383.15 K, and kept in a vacuum desiccator over P_2O_5 for at least 72 h before use. The salts were recrystallized twice in triply distilled water, dried at 423.15 K for at least 3 h, and then kept over P_2O_5 in a vacuum desiccator at room temperature for a minimum of 48 h prior to their use. Stock solutions of 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl and 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KNO_3 were prepared in triply distilled water and were used as solvents for the preparation of amino acid and peptide solutions. The specific electrical conductivity of triply distilled water used was less than $18\cdot10^{-6}\ \Omega^{-1}\cdot\text{cm}^{-1}$. All the solutions were stored in special airtight bottles to avoid the exposure of solutions to air and evaporation.

An ultrasonic interferometer (Mittal model M-77, India) based on the variable-path principle was used for the measurement of the ultrasonic velocity at a frequency of 4 MHz at different temperatures using a method described elsewhere.[16,17,19] An average of 10 readings was taken as a final value of the ultrasonic velocity. Water from a thermostat was circulated through a brass jacket surrounding the cell and the quartz crystal. The jacket was well insulated, and the temperature of the solution under study was maintained to an uncertainty of 0.01 K. The instrument was tested with the ultrasonic velocity values of triple-distilled water at different temperatures taken from the literature.[20]

The densities of solutions were measured with a pyknometer using a method described elsewhere.[14,15,19] All mass quantities were corrected for buoyancy. The densities of toluene at various required temperatures were taken from the literature for calibration purposes.[21] The thermostatted water bath used for measurements of ultrasonic velocity and the thermostatted paraffin bath used for measurements of density were maintained at a desired temperature (± 0.01 K) for about 30 min prior to recording of readings at each temperature of study. Several very close readings of density calculated at each temperature were averaged.

The uncertainties in measurements of the ultrasonic velocity and density values were ascertained by comparing the experimental values with corresponding literature values at different temperatures for water. The measured values of the ultrasonic velocity of water were found to be (1496.8, 1519.9, and 1536.4) $\text{m}\cdot\text{s}^{-1}$ at (298.15, 308.15, and 318.15) K, respectively, whereas the corresponding literature values[20] are (1496.687, 1519.808, and 1536.409) $\text{m}\cdot\text{s}^{-1}$. The experimental values of the density of water were found to be (0.9971, 0.9942, 0.9903, and 0.9879) $\text{g}\cdot\text{cm}^{-3}$ at (298.15, 308.15, 318.15, and 323.15) K, respectively,

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* To whom correspondence should be addressed. E-mail: rz1@rediffmail.com. Phone: +91 571 2703515.

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Table 1. Ultrasonic Velocity Values u as Functions of Molality m and Temperature T

m	$u/(\mathrm{m \cdot s^{-1}})$					
$\mathrm{mol \cdot kg^{-1}}$	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
L-Histidine in 2 $\mathrm{mol \cdot L^{-1}}$ KCl						
0.0000	1592.8	1600.4	1608.0	1614.0	1617.2	1622.0
0.0277	1595.6	1604.0	1610.4	1616.8	1621.4	1625.2
0.0555	1597.2	1605.6	1612.8	1618.4	1623.4	1626.4
0.0836	1599.2	1607.6	1615.2	1620.8	1624.8	1628.4
0.1117	1600.8	1609.6	1617.2	1622.4	1626.4	1630.4
0.1400	1602.8	1611.6	1618.8	1623.6	1628.0	1632.0
0.1686	1604.8	1613.6	1620.4	1625.6	1630.4	1634.0
0.1974	1606.4	1615.6	1622.4	1626.8	1632.0	1636.0
0.2263	1608.4	1618.0	1624.4	1629.2	1633.6	1637.6
L-Histidine in 2 $\mathrm{mol \cdot L^{-1}}$ KNO_3						
0.0000	1558.8	1566.8	1572.8	1577.6	1582.0	1586.4
0.0270	1562.4	1570.0	1576.8	1581.6	1586.0	1589.6
0.0541	1564.4	1572.0	1578.4	1583.6	1587.6	1591.6
0.0815	1566.8	1574.0	1580.4	1585.6	1589.2	1592.8
0.1090	1568.8	1576.0	1582.4	1587.2	1590.8	1594.8
0.1367	1570.8	1578.0	1584.4	1589.2	1592.8	1596.0
0.1645	1573.2	1580.4	1586.4	1591.2	1594.8	1598.0
0.1926	1575.2	1582.4	1588.4	1593.2	1596.8	1600.0
0.2207	1577.6	1584.4	1590.8	1595.6	1598.8	1602.4
L-Glutamic Acid in 2 $\mathrm{mol \cdot L^{-1}}$ KCl						
0.0000	1592.8	1600.4	1608.0	1614.0	1617.2	1622.0
0.0092	1594.0	1600.8	1608.4	1614.4	1617.8	1622.4
0.0184	1594.4	1601.2	1608.8	1614.8	1618.4	1623.2
0.0277	1594.8	1601.6	1609.2	1615.2	1618.8	1624.0
0.0369	1595.2	1602.0	1609.6	1615.6	1619.6	1624.8
0.0462	1596.0	1602.4	1610.0	1616.0	1620.0	1625.6
0.0555	1596.4	1603.2	1610.4	1616.8	1620.4	1626.4
L-Glutamic Acid in 2 $\mathrm{mol \cdot L^{-1}}$ KNO_3						
0.0000	1558.8	1566.8	1572.8	1577.6	1582.0	1586.4
0.0090	1559.2	1567.6	1573.2	1578.8	1583.6	1587.2
0.0180	1560.4	1568.8	1574.4	1579.6	1584.8	1588.0
0.0270	1561.2	1569.2	1575.6	1580.8	1585.6	1588.8
0.0360	1562.0	1570.4	1576.8	1582.0	1586.4	1589.0
0.0450	1562.8	1571.2	1577.6	1583.2	1587.6	1590.4
0.0541	1563.6	1572.2	1578.0	1584.0	1588.4	1591.2
L-Tryptophan in 2 $\mathrm{mol \cdot L^{-1}}$ KCl						
0.0000	1592.8	1600.4	1608.0	1614.0	1617.2	1622.0
0.0092	1593.6	1601.6	1608.8	1614.8	1620.0	1623.6
0.0138	1594.0	1602.0	1609.6	1615.2	1620.4	1624.0
0.0184	1594.4	1603.2	1610.0	1615.6	1620.8	1624.4
0.0231	1595.2	1604.0	1610.4	1616.0	1621.6	1625.2
0.0277	1596.0	1604.8	1610.8	1616.8	1622.4	1626.0
0.0323	1596.8	1605.6	1611.6	1617.6	1622.8	1626.4
0.0370	1597.6	1606.4	1612.0	1618.4	1623.6	1627.6
L-Tryptophan in 2 $\mathrm{mol \cdot L^{-1}}$ KNO_3						
0.0000	1558.8	1566.8	1572.6	1577.6	1582.0	1586.4
0.0092	1560.8	1567.6	1573.0	1578.0	1582.8	1586.8
0.0135	1561.2	1568.0	1573.6	1578.4	1583.2	1587.2
0.0180	1562.0	1568.4	1574.8	1579.2	1584.0	1587.6
0.0225	1562.6	1569.2	1575.6	1580.0	1584.4	1588.4
0.0270	1563.2	1570.0	1576.0	1580.8	1585.2	1589.2
0.0315	1564.0	1570.8	1576.8	1581.2	1586.0	1590.0
0.0361	1564.8	1571.6	1578.0	1582.0	1586.8	1590.8
Glycylglycine in 2 $\mathrm{mol \cdot L^{-1}}$ KCl						
0.0000	1592.8	1600.4	1608.0	1614.0	1617.2	1622.0
0.0184	1594.0	1601.2	1609.2	1614.9	1621.6	1625.2
0.0369	1596.4	1603.2	1610.4	1616.4	1622.4	1626.0
0.0554	1598.5	1605.6	1612.7	1617.7	1623.6	1627.6
0.0740	1599.6	1607.5	1613.2	1618.4	1624.4	1628.4
0.0927	1600.8	1608.8	1614.4	1620.2	1626.0	1629.2
0.1114	1602.4	1609.6	1615.6	1622.4	1627.2	1630.4
0.1302	1603.2	1610.4	1616.8	1623.3	1628.0	1630.8
0.1491	1604.4	1611.2	1617.8	1624.4	1628.8	1632.4
Glycylglycine in 2 $\mathrm{mol \cdot L^{-1}}$ KNO_3						
0.0000	1558.8	1566.8	1572.8	1577.6	1582.0	1586.4
0.0180	1561.4	1568.4	1575.6	1580.4	1585.2	1589.6
0.0360	1562.6	1569.6	1576.4	1582.0	1586.0	1590.4
0.0541	1563.5	1571.6	1577.2	1582.8	1587.2	1591.6
0.0722	1564.8	1572.8	1578.8	1584.0	1588.4	1592.8
0.0904	1566.4	1574.6	1580.0	1585.2	1590.0	1594.8
0.1087	1567.6	1576.0	1581.6	1586.8	1591.6	1595.6
0.1270	1569.0	1576.8	1582.8	1588.0	1593.2	1596.4
0.1454	1570.4	1578.0	1584.4	1590.0	1594.4	1597.6

Table 2. Density Values ρ as Functions of Molality m and Temperature T

m	$\rho\cdot10^{-3}/(\mathrm{kg\cdot m^{-3}})$					
$\mathrm{mol\cdot kg^{-1}}$	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
L-Histidine in 2 $\mathrm{mol\cdot L^{-1}}$ KCl						
0.0000	1.0877	1.0857	1.0836	1.0813	1.0788	1.0761
0.0277	1.0883	1.0865	1.0844	1.0821	1.0795	1.0768
0.0555	1.0896	1.0877	1.0857	1.0834	1.0809	1.0783
0.0836	1.0909	1.0890	1.0870	1.0847	1.0823	1.0796
0.1117	1.0926	1.0906	1.0885	1.0861	1.0837	1.0810
0.1400	1.0944	1.0923	1.0901	1.0878	1.0853	1.0827
0.1686	1.0953	1.0933	1.0912	1.0889	1.0864	1.0838
0.1974	1.0966	1.0945	1.0922	1.0898	1.0873	1.0847
0.2263	1.0979	1.0958	1.0935	1.0911	1.0886	1.0860
L-Histidine in 2 $\mathrm{mol\cdot L^{-1}}$ KNO_3						
0.0000	1.1150	1.1125	1.1098	1.1070	1.1040	1.1009
0.0270	1.1159	1.1134	1.1107	1.1078	1.1048	1.1017
0.0541	1.1173	1.1147	1.1120	1.1090	1.1060	1.1028
0.0815	1.1187	1.1160	1.1132	1.1102	1.1072	1.1040
0.1090	1.1194	1.1170	1.1143	1.1114	1.1082	1.1049
0.1367	1.1204	1.1178	1.1150	1.1122	1.1092	1.1060
0.1645	1.1220	1.1196	1.1169	1.1140	1.1110	1.1077
0.1926	1.1230	1.1204	1.1177	1.1148	1.1118	1.1087
0.2207	1.1247	1.1221	1.1194	1.1166	1.1136	1.1104
L-Glutamic Acid in 2 $\mathrm{mol\cdot L^{-1}}$ KCl						
0.0000	1.0877	1.0857	1.0836	1.0813	1.0788	1.0761
0.0092	1.0879	1.0859	1.0837	1.0815	1.0790	1.0765
0.0184	1.0881	1.0861	1.0840	1.0817	1.0793	1.0767
0.0277	1.0884	1.0865	1.0844	1.0822	1.0797	1.0771
0.0369	1.0887	1.0868	1.0847	1.0825	1.0800	1.0774
0.0462	1.0893	1.0875	1.0855	1.0833	1.0808	1.0781
0.0555	1.0902	1.0883	1.0862	1.0839	1.0815	1.0788
L-Glutamic Acid in 2 $\mathrm{mol\cdot L^{-1}}$ KNO_3						
0.0000	1.1150	1.1125	1.1098	1.1070	1.1040	1.1009
0.0090	1.1155	1.1130	1.1104	1.1076	1.1047	1.1016
0.0180	1.1160	1.1135	1.1108	1.1080	1.1050	1.1019
0.0270	1.1166	1.1141	1.1114	1.1086	1.1056	1.1026
0.0360	1.1171	1.1147	1.1120	1.1092	1.1062	1.1032
0.0450	1.1174	1.1149	1.1122	1.1094	1.1064	1.1034
0.0541	1.1184	1.1159	1.1132	1.1104	1.1074	1.1042
L-Tryptophan in 2 $\mathrm{mol\cdot L^{-1}}$ KCl						
0.0000	1.0877	1.0857	1.0836	1.0813	1.0788	1.0761
0.0092	1.0879	1.0860	1.0838	1.0816	1.0791	1.0764
0.0138	1.0881	1.0862	1.0841	1.0819	1.0794	1.0767
0.0184	1.0882	1.0864	1.0843	1.0821	1.0796	1.0770
0.0231	1.0886	1.0867	1.0846	1.0823	1.0798	1.0771
0.0277	1.0890	1.0870	1.0847	1.0824	1.0799	1.0773
0.0323	1.0894	1.0873	1.0851	1.0828	1.0803	1.0777
0.0370	1.0895	1.0874	1.0853	1.0829	1.0805	1.0779
L-Tryptophan in 2 $\mathrm{mol\cdot L^{-1}}$ KNO_3						
0.0000	1.1150	1.1125	1.1098	1.1070	1.1040	1.1009
0.0092	1.1153	1.1127	1.1100	1.1072	1.1042	1.1011
0.0135	1.1156	1.1131	1.1104	1.1076	1.1046	1.1015
0.0180	1.1157	1.1133	1.1106	1.1078	1.1048	1.1017
0.0225	1.1161	1.1135	1.1108	1.1080	1.1050	1.1018
0.0270	1.1163	1.1138	1.1111	1.1083	1.1053	1.1021
0.0315	1.1164	1.1139	1.1113	1.1084	1.1054	1.1023
0.0361	1.1169	1.1143	1.1115	1.1086	1.1056	1.1024
Glycylglycine in 2 $\mathrm{mol\cdot L^{-1}}$ KCl						
0.0000	1.0877	1.0857	1.0836	1.0813	1.0788	1.0761
0.0184	1.0881	1.0862	1.0841	1.0819	1.0795	1.0769
0.0369	1.0890	1.0871	1.0850	1.0828	1.0804	1.0778
0.0554	1.0902	1.0881	1.0859	1.0836	1.0812	1.0786
0.0740	1.0911	1.0890	1.0868	1.0845	1.0820	1.0794
0.0927	1.0923	1.0899	1.0875	1.0852	1.0827	1.0802
0.1114	1.0928	1.0905	1.0881	1.0857	1.0832	1.0807
0.1302	1.0935	1.0915	1.0893	1.0870	1.0845	1.0819
0.1491	1.0935	1.0922	1.0900	1.0877	1.0852	1.0826
Glycylglycine in 2 $\mathrm{mol\cdot L^{-1}}$ KNO_3						
0.0000	1.1150	1.1125	1.1098	1.1070	1.1040	1.1009
0.0180	1.1156	1.1130	1.1104	1.1076	1.1046	1.1015
0.0360	1.1161	1.1137	1.1111	1.1083	1.1053	1.1022
0.0541	1.1171	1.1148	1.1123	1.1096	1.1067	1.1035
0.0722	1.1181	1.1157	1.1131	1.1103	1.1073	1.1042
0.0904	1.1192	1.1166	1.1139	1.1111	1.1081	1.1050
0.1087	1.1198	1.1174	1.1148	1.1120	1.1090	1.1058
0.1270	1.1211	1.1185	1.1158	1.1129	1.1099	1.1068
0.1454	1.1216	1.1194	1.1170	1.1144	1.1117	1.1089

Table 3. Least Squares Fit Coefficients of the Ultrasonic Velocity Equation, $u = a + a_1(m/m_0)$, as a Function of Temperature

T/K	a/($\text{m}\cdot\text{s}^{-1}$)	a_1/($\text{m}\cdot\text{s}^{-1}$)	$\sigma_{[u]}$/($\text{m}\cdot\text{s}^{-1}$)
L-Histidine in 2 $\text{mol}\cdot\text{L}^{-1}$ KCl			
298.15	1593.37	66.93	0.29
303.15	1601.27	73.77	0.44
308.15	1608.66	70.92	0.47
313.15	1614.81	63.62	0.50
318.15	1618.84	67.14	0.81
323.15	1622.70	66.93	0.38
L-Histidine in 2 $\text{mol}\cdot\text{L}^{-1}$ KNO_3			
298.15	1559.72	81.64	0.45
303.15	1567.50	77.54	0.35
308.15	1573.92	76.56	0.56
313.15	1578.89	75.83	0.64
318.15	1583.20	71.01	0.61
323.15	1587.26	67.15	0.53
L-Glutamic Acid in 2 $\text{mol}\cdot\text{L}^{-1}$ KCl			
298.15	1593.13	60.13	0.23
303.15	1600.33	47.82	0.13
308.15	1608.00	43.19	0.01
313.15	1613.93	47.83	0.13
318.15	1617.26	58.60	0.11
323.15	1621.79	81.77	0.12
L-Glutamic Acid in 2 $\text{mol}\cdot\text{L}^{-1}$ KNO_3			
298.15	1558.66	91.95	0.15
303.15	1566.82	96.71	0.16
308.15	1572.62	106.21	0.32
313.15	1577.60	120.49	0.14
318.15	1582.40	114.14	0.27
323.15	1586.38	86.41	0.24
L-Tryptophan in 2 $\text{mol}\cdot\text{L}^{-1}$ KCl			
298.15	1592.38	132.07	0.31
303.15	1600.11	167.82	0.22
308.15	1607.95	109.04	0.13
313.15	1613.68	117.31	0.29
318.15	1617.89	159.08	0.42
323.15	1622.02	142.67	0.22
L-Tryptophan in 2 $\text{mol}\cdot\text{L}^{-1}$ KNO_3			
298.15	1559.05	158.70	0.18
303.15	1566.37	141.25	0.42
308.15	1571.99	155.07	0.40
313.15	1577.07	131.02	0.33
318.15	1581.64	134.81	0.25
323.15	1585.78	127.71	0.41
Glycylglycine in 2 $\text{mol}\cdot\text{L}^{-1}$ KCl			
298.15	1593.26	78.93	0.59
303.15	1600.67	77.58	0.82
308.15	1608.02	66.26	0.36
313.15	1613.68	72.72	0.38
318.15	1619.21	69.35	0.98
323.15	1623.43	61.49	0.73
Glycylglycine in 2 $\text{mol}\cdot\text{L}^{-1}$ KNO_3			
298.15	1559.49	75.29	0.37
303.15	1567.03	78.67	0.35
308.15	1573.45	74.47	0.43
313.15	1578.48	77.40	0.52
318.15	1582.84	80.34	0.49
323.15	1587.56	72.24	0.64

Table 4. Least-Square Fit Coefficients of the Density Equation, $\rho = b + b_1(m/m_0)$, as a Function of Temperature

T/K	b/($\text{g}\cdot\text{cm}^{-3}$)	$b_{1}\cdot10^{2}$/($\text{g}\cdot\text{cm}^{-3}$)	$\sigma_{[\rho]}\cdot10^{4}$/($\text{g}\cdot\text{cm}^{-3}$)
L-Histidine in 2 $\text{mol}\cdot\text{L}^{-1}$ KCl			
298.15	1.0872	4.750	3.21
303.15	1.0854	4.650	2.56
308.15	1.0834	4.543	2.33
313.15	1.0811	4.502	2.49
318.15	1.0786	4.513	2.62
323.15	1.0759	4.560	2.68
L-Histidine in 2 $\text{mol}\cdot\text{L}^{-1}$ KNO_3			
298.15	1.1149	4.301	2.49
303.15	1.1124	4.289	2.37
308.15	1.1096	4.429	2.57
313.15	1.1067	4.314	2.62
318.15	1.1037	4.314	2.73
323.15	1.1005	4.278	2.86
L-Glutamic Acid in 2 $\text{mol}\cdot\text{L}^{-1}$ KCl			
298.15	1.0874	4.211	2.83
303.15	1.0854	4.520	2.66
308.15	1.0833	4.674	2.66
313.15	1.0810	4.712	2.35
318.15	1.0785	4.790	2.44
323.15	1.0760	4.635	2.05
L-Glutamic Acid in 2 $\text{mol}\cdot\text{L}^{-1}$ KNO_3			
298.15	1.1149	5.986	1.47
303.15	1.1125	6.025	1.52
308.15	1.1098	5.946	1.56
313.15	1.1070	5.946	1.56
318.15	1.1040	5.867	1.69
323.15	1.1010	5.866	1.37
L-Tryptophan in 2 $\text{mol}\cdot\text{L}^{-1}$ KCl			
298.15	1.0875	5.400	1.78
303.15	1.0856	4.960	0.87
308.15	1.0835	4.808	0.94
313.15	1.0813	4.471	0.67
318.15	1.0787	4.629	0.71
323.15	1.0760	5.004	1.14
L-Tryptophan in 2 $\text{mol}\cdot\text{L}^{-1}$ KNO_3			
298.15	1.1149	5.145	1.05
303.15	1.1124	5.044	0.92
308.15	1.1097	4.999	0.78
313.15	1.1069	4.721	0.83
318.15	1.1040	4.565	1.40
323.15	1.1008	4.459	0.82
Glycylglycine in 2 $\text{mol}\cdot\text{L}^{-1}$ KCl			
298.15	1.0875	4.641	2.65
303.15	1.0856	4.516	1.35
308.15	1.0834	4.383	1.41
313.15	1.0812	4.320	1.52
318.15	1.0788	4.266	1.49
323.15	1.0761	4.329	1.20
Glycylglycine in 2 $\text{mol}\cdot\text{L}^{-1}$ KNO_3			
298.15	1.1147	4.807	2.33
303.15	1.1122	4.862	1.62
308.15	1.1095	4.954	1.78
313.15	1.1067	4.991	2.38
318.15	1.1037	5.092	3.23
323.15	1.1005	5.193	4.09

whereas the corresponding literature values[22] are (0.997045, 0.994032, 0.990213, and 0.988036) $\text{g}\cdot\text{cm}^{-3}$. The uncertainties in the ultrasonic velocity and density and molal concentration values have been found to be within 0.2 $\text{m}\cdot\text{s}^{-1}$, $1.0\cdot10^{-4}$ $\text{g}\cdot\text{cm}^{-3}$, and $1.0\cdot10^{-4}$ $\text{mol}\cdot\text{kg}^{-1}$, respectively.

Results and Discussion

The ultrasonic velocity and density values of the L-histidine or L-glutamic acid or L-tryptophan or glycylglycine + 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl or 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KNO_3 systems have been measured experimentally as a function of molality of amino acid/peptide at T= (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K. The measured values of u and ρ have been listed in Tables 1 and 2, respectively. The ultrasonic velocity and density data have been least-squares fitted to the following equations

$$u/\text{m}\cdot\text{s}^{-1} = a + a_1(m/m_0) \tag{1}$$

$$\rho/\text{g}\cdot\text{cm}^{-3} = b + b_1(m/m_0) \tag{2}$$

where a, a_1 and b, b_1 are the fitted coefficients. The $m_0 = 1$ $\text{mol}\cdot\text{kg}^{-1}$, and m is molality of solution. The standard deviation, σ, is defined as

Table 5. Isentropic Compressibility Values κ_s as Functions of Solute Concentration and Temperature

m	$\kappa_s\cdot 10^{11}/(\mathrm{m^2\cdot N^{-1}})$					
$\mathrm{mol\cdot kg^{-1}}$	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
			L-Histidine in 2 $\mathrm{mol\cdot L^{-1}}$ KCl			
0.0000	36.24	35.96	35.69	35.50	35.44	35.32
0.0277	36.09	35.77	35.56	35.35	35.23	35.16
0.0555	35.98	35.66	35.41	35.24	35.10	35.06
0.0836	35.84	35.53	35.26	35.09	35.00	34.93
0.1117	35.72	35.39	35.13	34.98	34.88	34.80
0.1400	35.57	35.25	35.01	34.87	34.76	34.68
0.1686	35.45	35.13	34.90	34.75	34.63	34.56
0.1974	35.34	35.04	34.78	34.67	34.53	34.44
0.2263	35.21	34.86	34.66	34.53	34.42	34.34
			L-Histidine in 2 $\mathrm{mol\cdot L^{-1}}$ KNO_3			
0.0000	36.91	36.62	36.42	36.29	36.19	36.09
0.0270	36.71	36.44	36.21	36.09	35.98	35.92
0.0541	36.57	36.30	36.10	35.96	35.87	35.80
0.0815	36.41	36.17	35.97	35.83	35.76	35.70
0.1090	36.30	36.04	35.84	35.72	35.66	35.58
0.1367	36.17	35.93	35.73	35.60	35.53	35.49
0.1645	36.01	35.76	35.58	35.45	35.39	35.35
0.1926	35.87	35.64	35.46	35.34	35.27	35.23
0.2207	35.72	35.50	35.30	35.18	35.13	35.07
			L-Glutamic Acid in 2 $\mathrm{mol\cdot L^{-1}}$ KCl			
0.0000	36.24	35.96	35.69	35.50	35.44	35.32
0.0092	36.18	35.94	35.67	35.48	35.41	35.29
0.0184	36.15	35.91	35.64	35.45	35.37	35.25
0.0277	36.12	35.88	35.61	35.42	35.34	35.20
0.0369	36.10	35.85	35.58	35.39	35.30	35.16
0.0462	36.04	35.81	35.54	35.35	35.25	35.10
0.0555	35.98	35.75	35.50	35.29	35.21	35.04
			L-Glutamic Acid in 2 $\mathrm{mol\cdot L^{-1}}$ KNO_3			
0.0000	36.91	36.62	36.42	36.29	36.19	36.09
0.0092	36.88	36.56	36.39	36.22	36.10	36.03
0.0180	36.80	36.49	36.32	36.17	36.03	35.99
0.0270	36.74	36.45	36.24	36.10	35.98	35.93
0.0360	36.69	36.38	36.17	36.02	35.92	35.90
0.0450	36.64	36.33	36.13	35.96	35.86	35.83
0.0541	36.57	36.26	36.07	35.89	35.79	35.77
			L-Tryptophan in 2 $\mathrm{mol\cdot L^{-1}}$ KCl			
0.0000	36.24	35.96	35.69	35.50	35.44	35.32
0.0092	36.19	35.90	35.65	35.46	35.31	35.24
0.0138	36.17	35.87	35.60	35.43	35.28	35.21
0.0184	36.15	35.81	35.58	35.40	35.26	35.19
0.0231	36.10	35.77	35.55	35.38	35.22	35.15
0.0277	36.05	35.72	35.53	35.34	35.18	35.11
0.0323	36.00	35.67	35.48	35.29	35.15	35.08
0.0370	35.96	35.64	35.46	35.26	35.11	35.02
			L-Tryptophan in 2 $\mathrm{mol\cdot L^{-1}}$ KNO_3			
0.0000	36.91	36.62	36.42	36.29	36.19	36.09
0.0090	36.80	36.57	36.41	36.27	36.15	36.07
0.0135	36.78	36.54	36.37	36.24	36.12	36.04
0.0180	36.73	36.51	36.31	36.20	36.07	36.01
0.0225	36.69	36.47	36.26	36.15	36.05	35.97
0.0270	36.66	36.42	36.23	36.11	36.00	35.93
0.0315	36.62	36.38	36.19	36.08	35.96	35.88
0.0361	36.56	36.33	36.13	36.04	35.92	35.84
			Glycylglycine in 2 $\mathrm{mol\cdot L^{-1}}$ KCl			
0.0000	36.24	35.96	35.69	35.50	35.44	35.32
0.0184	36.17	35.91	35.62	35.44	35.23	35.16
0.0369	36.03	35.79	35.54	35.35	35.16	35.09
0.0554	35.90	35.65	35.41	35.26	35.09	35.00
0.0740	35.82	35.54	35.36	35.20	35.02	34.94
0.0927	35.72	35.45	35.28	35.10	34.93	34.86
0.1114	35.64	35.39	35.21	34.99	34.87	34.81
0.1302	35.58	35.33	35.12	34.91	34.79	34.75
0.1491	35.50	35.27	35.05	34.84	34.73	34.66
			Glycylglycine in 2 $\mathrm{mol\cdot L^{-1}}$ KNO_3			
0.0000	36.91	36.62	36.42	36.29	36.19	36.09
0.0180	36.77	36.52	36.28	36.15	36.03	35.93
0.0360	36.69	36.45	36.22	36.05	35.97	35.87
0.0541	36.62	36.32	36.14	35.97	35.87	35.77
0.0722	36.52	36.23	36.04	35.90	35.79	35.70
0.0904	36.41	36.12	35.96	35.82	35.70	35.58
0.1087	36.34	36.03	35.86	35.71	35.59	35.52
0.1270	36.23	35.96	35.77	35.63	35.49	35.45
0.1454	36.15	35.87	35.66	35.49	35.38	35.33

$$\sigma = \left(\sum_{i=1}^{N}(x_i(\text{observed}) - x_i(\text{smoothed}))^2/(N - m)\right)^{1/2} \tag{3}$$

where m is the number of the coefficients determined by the least-squares method. The fitted coefficients along with their standard deviations are listed in Tables 3 and 4. Table 1 reveals that the ultrasonic velocity values increase with an increase in molality of amino acid/peptide in the 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl or KNO_3 solution. Amino acid and peptide molecules in aqueous solution essentially behave as zwitterions having NH_3^+ and COO^- groups at two ends of the molecule. The K^+, Cl^-, and NO_3^- ions furnished by KCl and KNO_3 in solutions may interact electrostatically with NH_3^+ and COO^- end groups of zwitterions. The water dipoles may interact with the ions K^+, Cl^- and NO_3^- and zwitterion end groups NH_3^+ and COO^-. These interactions comprehensively introduce the cohesion into solutions under study. These cohesive forces may further have enhanced on successive addition of amino acid/peptide amount in solutions.[23−28] The ultrasonic velocity values for the studied systems increase with an increase in temperature. The rise in temperature may cause the thermal rupture of an icelike open structure to the close packed structure of water. It seems that the cohesion factor dominates over the thermal expansion factor in solutions with an increase in temperature.[16,26,29,30]

The isentropic compressibility values for the amino acid or peptide + 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl or KNO_3 solution have been calculated from the ultrasonic velocity and density values using the Newton−Laplace relation

$$\kappa_s = 1/\rho \cdot u^2 \tag{4}$$

The κ_s values as functions of molality of amino acid or peptide and temperature have been listed in Table 5. The κ_s values decrease with an increase in molality of solute as well as temperature. The decrease in isentropic compressibility values with an increase in molality of L-histidine, L-glutamic acid, L-tryptophan, and glycylglycine in 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous solutions of KCl and KNO_3 may be due to (i) an increase in the number of molecules/zwitterions in solution and (ii) the probable formation of “zwitterions−water dipoles” and “zwitterions−ions” entities in solution. The decrease in isentropic compressibility values with an increase in temperature in all the systems under investigation may be attributed to the corresponding decrease of the relaxational part of compressibility κ_{relax}, which is dominant over the corresponding increase of instantaneous part of compressibility κ_∞.[29,30]

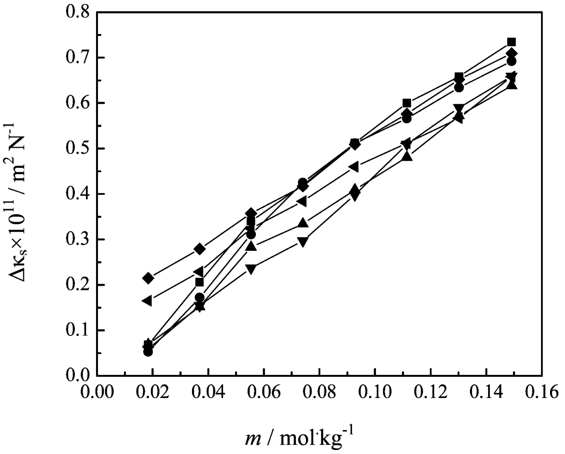

Figure 1. Plot of change in isentropic compressibility, $\Delta\kappa_s$, against molality of glycylglycine in 2 $\text{mol}\cdot\text{L}^{-1}$ KCl solution at temperatures: ■, $T = 298.15$ K; ●, $T = 303.15$ K; ▲, $T = 308.15$ K; ▼, $T = 313.15$ K; ♦, $T = 318.15$ K; and solid left triangle, $T = 323.15$ K.

The isentropic compressibility values of 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl and 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KNO_3 solutions are less than that of water in the temperature range of $T = (298.15$ to $323.15)$ K. For instance, at 298.15 K the isentropic compressibility values of 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous solution of KCl and 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous solution of KNO_3 are $36.24\cdot10^{-11}$ $m^2\cdot N^{-1}$ and $36.91\cdot10^{-11}$ $m^2\cdot N^{-1}$, respectively, whereas that of water is $44.773\cdot10^{-11}$ $m^2\cdot N^{-1}$.[31] The smaller values of κ_s for the said aqueous electrolytic solutions than that of water may be attributed to ions−water dipoles and ions−zwitterions interactions in the solutions, which ultimately may lead to an overall increase in cohesive forces in solutions. The value of isentropic compressibility of 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl solution ($36.24\cdot10^{-11}$ $m^2\cdot N^{-1}$ at 298.15 K) is less than that of 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KNO_3 solution ($36.9\cdot10^{-11}$ $m^2\cdot N^{-1}$ at 298.15 K) at all the temperatures of study. This trend may be attributed to the effect of smaller size of the Cl^- ion than that of the NO_3^- ion. The Cl^- ion is a stronger structure making ion than that of the NO_3^- ion. The K^+ is a common ion in both the electrolytes. Further, a decrease in κ_s value on a successive increase in amino acid and peptide molecules in the 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl or KNO_3 solution may be due to (i) an increase in the number of incompressible amino acid and peptide molecules/zwitterions in the solutions and (ii) an increase in the cohesive forces in solution on account of the corresponding increase in attractive forces between ions and zwitterions.

The change in isentropic compressibility ($\Delta\kappa_s = \kappa_0 - \kappa_s$) values for the amino acid or peptide + 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl or KNO_3 solution have been calculated. The calculated values of $\Delta\kappa_s$ are listed in Table S1 of the Supporting Information. The trends of variation of $\Delta\kappa_s$ values with molality of glycylglycine in 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl at all temperatures of study are displayed in Figure 1. The $\Delta\kappa_s$ values exhibit an increasing trend of variation with an increase in molality of amino acid or peptide in the solutions. However, an irregular trend of variation of $\Delta\kappa_s$ with an increase in temperature has been observed in both the solvents, i.e., 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl and 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KNO_3 solutions. Such an increase in $\Delta\kappa_s$ values with an increase in amino acid/peptide/zwitterions concentration in the solutions may be attributed to an overall increase in the cohesive force in the solutions.

Conclusions

The ultrasonic velocity values for L-histidine or L-glutamic acid or L-tryptophan or glycylglycine + 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KCl or 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous KNO_3 solution increase with an increase in molality of solute as well as temperature from $T = (298.15$ to $323.15)$ K. The density values increase with an increase in molality of solute and decrease with an increase in temperature for the systems under investigation. The isentropic compressibilities decrease with an increase in the amino acid/dipeptide concentration as well as temperature.

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Supporting Information Available:

The calculated change in isentropic compressibility ($\Delta\kappa_s = \kappa_0 - \kappa_s$) values for the amino acid or peptide + 2 $\text{mol}\cdot\text{L}^{-1}$ aqueous

KCl or KNO_3 solution are listed in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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