Ultrasonic Velocities and Densities of L-Phenylalanine, L-Leucine, L-Glutamic Acid, and L-Proline + 2 mol·L^{-1} Aqueous NaCl and 2 mol·L^{-1} Aqueous $NaNO_3$ Solutions from (298.15 to 328.15) K

Riyazuddeen* and Sadaf Afrin

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

Ultrasonic velocity and density values of L-phenylalanine, L-leucine, L-glutamic acid, and L-proline + 2 mol·L^{-1} aqueous NaCl and 2 mol·L^{-1} aqueous $NaNO_3$ solutions have been measured for several molal concentrations of amino acids at different temperatures from T = (298.15 to 328.15) K. The isentropic compressibility values (κ_s) have been computed using the ultrasonic velocity and density data. The κ_s values decrease with an increase in the molal concentration of amino acids as well as with temperature. The trends of variation of κ_s with the variation in molal concentration of amino acids as well as with temperature have been discussed in terms of various interactions operative in solutions.

Introduction

L-α-Amino acids are involved in many biological processes in the human body like transmission, decarboxylation, and metabolism. They also participate in intracellular metabolism and operate specific transport systems of the plasma membrane.[1] The effects of salts on the structure and function of proteins and nucleic acids in terms of their structure-making or breaking property have been studied by number of authors.[2−5] The study of salt−protein interactions provides an important insight into the conformational stability and unfolding behavior of globular proteins. One approach that reduces the degree of complexity in the study of salt−protein interactions and requires less complex measurement techniques is to study the interactions of protein model compounds, amino acids, and peptides in the salt solutions.[6−11] The ultrasonic velocity and its derived parameter isentropic compressibility are sensitive to structural changes that occur in solutions and to intermolecular or interionic interactions in solutions.[12−16]

The present work reports the ultrasonic velocity (u) and density (ρ) values of the amino acids: L-phenylalanine, L-leucine, L-glutamic acid, and L-proline in 2 mol·L^{-1} aqueous NaCl and 2 mol·L^{-1} aqueous $NaNO_3$ solutions as functions of amino acid concentration and temperatures of (298.15, 303.15, 308.15, 313.15, 318.15, 323.15, and 328.15) K. The isentropic compressibility values have been computed using the ultrasonic velocity and density data. The trends of variation of experimental and computed parameters with the variation in molal concentration of solute and temperature have been discussed in terms of various interactions operative in solutions.

Materials and Methods

The amino acids L-phenylalanine, L-leucine, L-glutamic acid, and L-proline, and the salts sodium chloride and sodium nitrate with minimum mass fraction purities of 0.99 used in this study were purchased from SRL (India) and E. Merck (India), respectively. The amino acids were recrystallized 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 to remove traces of water. 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 mol·L^{-1} aqueous NaCl and 2 mol·L^{-1} aqueous $NaNO_3$ were prepared using triply distilled water with a specific conductance less than $18 \cdot 10^{-6}\ \Omega^{-1} \cdot cm^{-1}$ and were used as solvents for the preparation of amino acid solutions of different molal concentrations. All solutions were stored in special airtight bottles to minimize the absorption of atmospheric moisture and carbon dioxide.

An ultrasonic interferometer (Mittal's model: M-77, India) based on the variable-path principle was used for the measurement of ultrasonic velocity at a frequency of 4 MHz at different temperatures using a method described elsewhere.[17,18] Water from an ultrathermostat (type U-10) was circulated through the 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 accuracy of ± 0.01°. An average of 10 readings was taken as a final value of ultrasonic velocity. 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 to minimize thermal fluctuations.

The densities of amino acid solutions were measured using a pycnometer by a method described elsewhere.[6,7,17] All mass quantities were corrected for buoyancy. The marks on the capillary were calibrated with water. The densities of water at different required temperatures were taken from literature for calibration purposes.[19] Several very close readings of density calculated at each temperature were averaged.

The uncertainties in measurements of the ultrasonic velocity[20] and density[19] values were ascertained by comparing the experimental values with corresponding literature values at different temperatures for water. The uncertainties in the ultrasonic velocity, density, and molal concentration values have

* Corresponding author. E-mail: rz1@rediffmail.com. Phone: +91 571 2703515.

10.1021/je900909s
Published on Web 03/31/2010

Table 1. Ultrasonic Velocities, *u*, as Functions of Solute Concentration, *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	T/K = 328.15
			L-Phenylalanine in 2 $\mathrm{mol \cdot L^{-1}}$ NaCl				
0.0000	1614.3	1620.9	1627.6	1633.7	1637.3	1640.5	1643.7
0.0187	1615.7	1622.3	1629.0	1635.9	1639.9	1642.9	1644.6
0.0374	1618.3	1624.9	1630.3	1636.8	1641.1	1644.1	1646.9
0.0562	1620.1	1627.1	1632.6	1638.7	1643.0	1646.4	1648.2
0.0751	1620.9	1628.5	1634.8	1639.7	1644.8	1647.0	1649.3
0.0941	1621.7	1628.9	1635.7	1640.9	1645.5	1648.2	1650.3
			L-Phenylalanine in 2 $\mathrm{mol \cdot L^{-1}}$ $NaNO_3$				
0.0000	1581.4	1588.6	1593.2	1596.3	1600.1	1604.3	1607.1
0.0180	1582.8	1589.6	1594.4	1599.0	1602.7	1606.1	1608.8
0.0362	1585.0	1592.7	1596.5	1600.9	1605.1	1608.4	1610.4
0.0543	1587.2	1594.9	1598.8	1603.9	1606.7	1610.1	1611.6
0.0726	1588.8	1596.5	1600.5	1605.5	1608.7	1610.9	1613.5
0.0909	1590.6	1599.1	1602.0	1606.1	1610.0	1612.8	1615.2
0.1094	1592.7	1600.7	1604.0	1608.3	1612.1	1614.3	1616.0
0.1280	1594.0	1603.5	1606.4	1610.3	1613.4	1616.3	1617.6
0.1465	1597.2	1605.6	1608.5	1612.4	1615.1	1617.9	1618.9
			L-Leucine in 2 $\mathrm{mol \cdot L^{-1}}$ NaCl				
0.0000	1614.3	1620.9	1627.6	1633.7	1637.3	1640.5	1642.7
0.0186	1619.0	1625.1	1631.9	1637.3	1640.9	1644.2	1646.7
0.0374	1620.3	1626.3	1633.7	1638.4	1642.7	1645.9	1648.0
0.0562	1621.5	1628.0	1634.6	1640.5	1644.2	1647.0	1649.6
0.0750	1623.5	1630.1	1636.8	1641.5	1645.7	1648.4	1650.5
0.0940	1626.0	1632.6	1638.0	1643.1	1648.0	1651.1	1652.4
0.1130	1628.9	1633.3	1639.7	1643.8	1648.8	1652.0	1654.3
			L-Leucine in 2 $\mathrm{mol \cdot L^{-1}}$ $NaNO_3$				
0.0000	1581.4	1588.6	1593.2	1596.3	1600.1	1604.3	1607.1
0.0182	1584.3	1590.7	1597.1	1600.7	1604.0	1606.3	1608.4
0.0364	1585.7	1591.9	1598.5	1601.9	1605.0	1607.2	1609.6
0.0547	1588.7	1594.7	1599.5	1603.9	1606.5	1608.7	1610.9
0.0731	1589.8	1595.8	1600.9	1605.0	1608.0	1610.3	1611.6
0.0915	1593.1	1597.0	1603.2	1606.3	1609.8	1611.7	1613.1
0.1101	1594.1	1598.2	1604.4	1608.0	1610.4	1612.9	1614.4
0.1287	1596.0	1601.0	1606.2	1610.0	1612.5	1614.9	1615.7
0.1474	1598.1	1603.7	1608.7	1611.2	1614.4	1615.7	1618.1
			L-Glutamic Acid in 2 $\mathrm{mol \cdot L^{-1}}$ NaCl				
0.0000	1614.3	1620.9	1627.6	1633.7	1637.3	1640.5	1643.7
0.0093	1615.4	1621.6	1628.0	1634.7	1638.0	1642.0	1644.4
0.0186	1615.7	1622.8	1628.5	1635.4	1638.8	1642.5	1645.2
0.0280	1616.4	1623.4	1629.2	1636.0	1639.5	1643.1	1645.7
0.0373	1616.7	1624.0	1630.0	1636.4	1640.4	1643.3	1645.5
0.0467	1617.2	1624.4	1630.5	1636.8	1640.8	1643.6	1646.0
0.0561	1618.0	1624.8	1631.2	1637.6	1641.6	1644.1	1646.8
			L-Glutamic Acid in 2 $\mathrm{mol \cdot L^{-1}}$ $NaNO_3$				
0.0000	1581.4	1588.6	1593.2	1596.3	1600.1	1604.3	1607.1
0.0091	1582.5	1589.6	1594.3	1597.6	1601.7	1605.1	1607.9
0.0182	1583.2	1590.7	1595.4	1598.8	1602.6	1606.4	1608.3
0.0272	1584.3	1591.6	1596.0	1600.0	1603.6	1607.1	1609.2
0.0364	1584.7	1592.7	1597.9	1601.3	1604.7	1608.0	1610.1
0.0455	1585.8	1593.5	1599.3	1602.4	1606.0	1608.9	1610.7
0.0546	1587.5	1594.7	1600.2	1604.1	1607.9	1609.7	1611.2
			L-Proline in 2 $\mathrm{mol \cdot L^{-1}}$ NaCl				
0.0000	1614.3	1620.9	1627.6	1633.7	1637.3	1640.5	1643.7
0.1893	1625.3	1631.3	1637.6	1641.6	1646.0	1649.7	1653.6
0.3854	1636.7	1643.2	1649.1	1655.1	1658.8	1662.0	1665.2
0.5881	1650.5	1656.3	1662.1	1666.1	1669.3	1671.2	1673.6
0.7988	1663.6	1668.4	1672.9	1676.9	1678.9	1682.1	1684.0
1.0166	1676.5	1681.2	1684.9	1688.3	1690.5	1692.0	1694.4
1.2426	1687.6	1691.4	1695.4	1699.0	1701.2	1702.8	1704.6
1.4782	1697.7	1701.7	1705.6	1709.2	1711.6	1712.8	1715.2
1.7234	1708.8	1713.2	1716.0	1720.0	1722.5	1724.0	1725.6
			L-Proline in 2 $\mathrm{mol \cdot L^{-1}}$ $NaNO_3$				
0.0000	1581.4	1588.6	1593.2	1596.3	1600.1	1604.3	1607.1
0.1841	1594.6	1600.3	1605.4	1609.8	1611.6	1614.0	1616.1
0.3748	1607.1	1612.9	1617.5	1620.8	1623.2	1625.2	1627.6
0.5725	1619.4	1624.4	1629.6	1633.2	1634.8	1637.6	1639.6
0.7773	1631.5	1636.7	1641.2	1644.8	1647.2	1649.1	1651.2
0.9898	1643.5	1648.9	1653.5	1657.5	1659.2	1661.5	1663.6
1.2110	1655.2	1659.6	1664.0	1667.6	1670.2	1672.4	1674.9
1.4404	1665.6	1670.2	1675.1	1678.9	1680.9	1683.1	1685.2
1.6789	1675.9	1680.9	1684.6	1688.7	1691.2	1693.2	1695.2

Table 2. Densities, ρ, as Functions of Solute Concentration, *m*, and Temperature, *T*

m	$\rho \cdot 10^{-3}/(\mathrm{kg \cdot m^{-3}})$						
$\mathrm{mol \cdot kg^{-1}}$	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 328.15
			L-Phenylalanine in 2 $\mathrm{mol \cdot L^{-1}}$ NaCl				
0.0000	1.0750	1.0730	1.0707	1.0683	1.0657	1.0631	1.0602
0.0187	1.0758	1.0735	1.0712	1.0688	1.0663	1.0637	1.0611
0.0374	1.0767	1.0746	1.0723	1.0699	1.0673	1.0647	1.0619
0.0562	1.0776	1.0756	1.0734	1.0711	1.0687	1.0660	1.0632
0.0751	1.0782	1.0762	1.0740	1.0717	1.0692	1.0666	1.0637
0.0941	1.0789	1.0770	1.0748	1.0725	1.0699	1.0671	1.0641
			L-Phenylalanine in 2 $\mathrm{mol \cdot L^{-1}}$ $NaNO_3$				
0.0000	1.1042	1.1017	1.0990	1.0963	1.0934	1.0904	1.0872
0.0180	1.1046	1.1019	1.0991	1.0965	1.0938	1.0911	1.0884
0.0362	1.1053	1.1025	1.0998	1.0973	1.0946	1.0921	1.0895
0.0543	1.1067	1.1041	1.1014	1.0988	1.0960	1.0932	1.0902
0.0726	1.1077	1.1050	1.1023	1.0996	1.0969	1.0944	1.0917
0.0909	1.1088	1.1061	1.1033	1.1008	1.0981	1.0955	1.0928
0.1094	1.1091	1.1065	1.1038	1.1012	1.0984	1.0957	1.0929
0.1280	1.1097	1.1072	1.1046	1.1021	1.0994	1.0967	1.0939
0.1465	1.1110	1.1086	1.1060	1.1035	1.1007	1.0980	1.0951
			L-Leucine in 2 $\mathrm{mol \cdot L^{-1}}$ NaCl				
0.0000	1.0750	1.0730	1.0707	1.0683	1.0657	1.0631	1.0602
0.0186	1.0753	1.0734	1.07129	1.0690	1.0665	1.0638	1.0609
0.0374	1.0757	1.0737	1.0715	1.0692	1.0668	1.0643	1.0616
0.0562	1.0762	1.0739	1.0715	1.0691	1.0667	1.0642	1.0616
0.0750	1.0768	1.0744	1.0720	1.0696	1.0673	1.0649	1.0625
0.0940	1.0774	1.0751	1.0727	1.0704	1.0680	1.0655	1.0631
0.1130	1.0776	1.0755	1.0732	1.0708	1.0683	1.0656	1.0629
			L-Leucine in 2 $\mathrm{mol \cdot L^{-1}}$ $NaNO_3$				
0.0000	1.1042	1.1017	1.0990	1.0963	1.0934	1.0904	1.0872
0.0182	1.1046	1.1024	1.1000	1.0972	1.0942	1.0910	1.0875
0.0364	1.1052	1.1028	1.1002	1.0974	1.0943	1.0910	1.0875
0.0547	1.1055	1.1029	1.1002	1.0973	1.0942	1.0910	1.0876
0.0731	1.1054	1.1028	1.1000	1.0971	1.0940	1.0908	1.0875
0.0915	1.1056	1.1029	1.1001	1.0972	1.0943	1.0912	1.0881
0.1101	1.1059	1.1033	1.1006	1.0977	1.0947	1.0915	1.0882
0.1287	1.1065	1.1040	1.1013	1.0984	1.0954	1.0923	1.0890
0.1474	1.1067	1.1041	1.1013	1.0984	1.0954	1.0922	1.0890
			L-Glutamic Acid in 2 $\mathrm{mol \cdot L^{-1}}$ NaCl				
0.0000	1.0750	1.0730	1.0707	1.0683	1.0657	1.0631	1.0602
0.0093	1.0753	1.0731	1.0708	1.0684	1.0659	1.0633	1.0606
0.0186	1.0760	1.0740	1.0717	1.0694	1.0668	1.0640	1.0611
0.0280	1.0767	1.0745	1.0722	1.0698	1.0672	1.0645	1.0617
0.0373	1.0770	1.0747	1.0724	1.0700	1.0675	1.0649	1.0623
0.0467	1.0774	1.0752	1.0729	1.0705	1.0680	1.0654	1.0627
0.0561	1.0781	1.0760	1.0737	1.0713	1.0687	1.0661	1.0634
			L-Glutamic Acid in 2 $\mathrm{mol \cdot L^{-1}}$ $NaNO_3$				
0.0000	1.1042	1.1017	1.0990	1.0963	1.0934	1.0904	1.0872
0.0091	1.1047	1.1022	1.0995	1.0965	1.0931	1.0895	1.0855
0.0182	1.1046	1.1019	1.0991	1.0963	1.0933	1.0903	1.0872
0.0272	1.1062	1.1033	1.1003	1.0972	1.0940	1.0907	1.0872
0.0364	1.1063	1.1036	1.1008	1.0980	1.0950	1.0920	1.0889
0.0455	1.1073	1.1048	1.1021	1.0993	1.0964	1.0934	1.0903
0.0546	1.1082	1.1056	1.1028	1.0998	1.0966	1.0931	1.0894
			L-Proline in 2 $\mathrm{mol \cdot L^{-1}}$ NaCl				
0.0000	1.0750	1.0730	1.0707	1.0683	1.0657	1.0631	1.0602
0.1893	1.0797	1.0774	1.0751	1.0727	1.0703	1.0678	1.0651
0.3854	1.0839	1.0817	1.0794	1.0770	1.0745	1.0718	1.0690
0.5881	1.0892	1.0870	1.0846	1.0822	1.0796	1.0770	1.0743
0.7988	1.0936	1.0915	1.0892	1.0868	1.0842	1.0815	1.0786
1.0166	1.0988	1.0965	1.0941	1.0915	1.0888	1.0859	1.0829
1.2426	1.1039	1.1016	1.0992	1.0967	1.0941	1.0914	1.0886
1.4782	1.1083	1.1056	1.1029	1.1003	1.0978	1.0953	1.0929
1.7234	1.1126	1.1101	1.1075	1.1049	1.1023	1.0997	1.0971
			L-Proline in 2 $\mathrm{mol \cdot L^{-1}}$ $NaNO_3$				
0.0000	1.1042	1.1017	1.0990	1.0963	1.0934	1.0904	1.0872
0.1841	1.1092	1.1066	1.1039	1.1009	1.0978	1.0945	1.0910
0.3748	1.1132	1.1102	1.1071	1.1041	1.1011	1.0980	1.0950
0.5725	1.1172	1.1143	1.1114	1.1085	1.1056	1.1027	1.0998
0.7773	1.1213	1.1186	1.1157	1.1127	1.1097	1.1065	1.1032
0.9898	1.1255	1.1227	1.1198	1.1168	1.1138	1.1108	1.1077
1.2110	1.1291	1.1263	1.1233	1.1204	1.1174	1.1145	1.1115
1.4404	1.1331	1.1302	1.1272	1.1243	1.1213	1.1182	1.1152
1.6789	1.1372	1.1344	1.1314	1.1284	1.1254	1.1223	1.1191

Table 3. Isentropic Compressibilities, κ_s, as Functions of Solute Concentration, *m*, and Temperature, *T*

m	$\kappa_s \cdot 10^{11}/(m^2 \cdot N^{1-})$						
$mol \cdot kg^{-1}$	*T*/K = 298.15	*T*/K = 303.15	*T*/K = 308.15	*T*/K = 313.15	*T*/K = 318.15	*T*/K = 323.15	*T*/K = 328.15
			L-Phenylalanine in 2 $mol \cdot L^{-1}$ NaCl				
0.0000	35.70	35.47	35.26	35.07	35.00	34.95	34.91
0.0187	35.61	35.39	35.18	34.96	34.88	34.83	34.84
0.0374	35.47	35.25	35.09	34.89	34.79	34.75	34.72
0.0562	35.36	35.12	34.95	34.77	34.66	34.61	34.62
0.0751	35.30	35.04	34.84	34.71	34.57	34.56	34.56
0.0941	35.24	35.00	34.77	34.63	34.52	34.50	34.51
			L-Phenylalanine in 2 $mol \cdot L^{-1}$ $NaNO_3$				
0.0000	36.22	35.97	35.85	35.80	35.72	35.64	35.61
0.0180	36.14	35.92	35.79	35.67	35.59	35.53	35.50
0.0362	36.01	35.76	35.68	35.56	35.46	35.40	35.39
0.0543	35.87	35.61	35.52	35.38	35.35	35.29	35.32
0.0726	35.76	35.50	35.41	35.28	35.23	35.21	35.19
0.0909	35.65	35.35	35.32	35.22	35.13	35.09	35.08
0.1094	35.54	35.27	35.21	35.11	35.03	35.02	35.03
0.1280	35.47	35.13	35.08	34.99	34.94	34.90	34.94
0.1465	35.28	34.99	34.95	34.86	34.83	34.79	34.84
			L-Leucine in 2 $mol \cdot L^{-1}$ NaCl				
0.0000	35.70	35.47	35.26	35.07	35.00	34.95	34.91
0.0186	35.48	35.27	35.05	34.89	34.83	34.77	34.76
0.0374	35.41	35.22	34.97	34.84	34.74	34.69	34.68
0.0562	35.34	35.13	34.93	34.76	34.68	34.64	34.62
0.0750	35.24	35.03	34.82	34.70	34.60	34.56	34.55
0.0940	35.11	34.90	34.74	34.61	34.47	34.43	34.45
0.1130	34.97	34.86	34.66	34.56	34.43	34.38	34.38
			L-Leucine in 2 $mol \cdot L^{-1}$ $NaNO_3$				
0.0000	36.22	35.97	35.85	35.80	35.72	35.64	35.61
0.0182	36.07	35.85	35.64	35.57	35.52	35.53	35.55
0.0364	35.99	35.78	35.57	35.51	35.47	35.48	35.49
0.0547	35.84	35.65	35.53	35.43	35.41	35.42	35.43
0.0731	35.79	35.61	35.47	35.38	35.35	35.36	35.41
0.0915	35.64	35.55	35.37	35.32	35.26	35.28	35.32
0.1101	35.59	35.49	35.30	35.23	35.22	35.22	35.26
0.1287	35.48	35.34	35.20	35.12	35.11	35.11	35.18
0.1474	35.38	35.22	35.09	35.07	35.03	35.07	35.08
			L-Glutamic Acid in 2 $mol \cdot L^{-1}$ NaCl				
0.0000	35.70	35.47	35.26	35.07	35.00	34.95	34.91
0.0093	35.64	35.44	35.23	35.02	34.97	34.88	34.87
0.0186	35.60	35.36	35.18	34.97	34.90	34.84	34.82
0.0280	35.55	35.31	35.14	34.93	34.86	34.79	34.78
0.0373	35.52	35.28	35.10	34.91	34.81	34.77	34.77
0.0467	35.49	35.25	35.06	34.87	34.78	34.75	34.73
0.0561	35.43	35.21	35.00	34.81	34.72	34.70	34.68
			L-Glutamic Acid in 2 $mol \cdot L^{-1}$ $NaNO_3$				
0.0000	36.22	35.97	35.85	35.80	35.72	35.64	35.61
0.0091	36.15	35.91	35.78	35.73	35.66	35.63	35.63
0.0182	36.12	35.87	35.75	35.69	35.61	35.54	35.56
0.0272	36.02	35.78	35.68	35.60	35.55	35.50	35.52
0.0364	36.00	35.72	35.58	35.52	35.46	35.42	35.43
0.0455	35.91	35.65	35.48	35.43	35.36	35.33	35.35
0.0546	35.81	35.57	35.41	35.34	35.28	35.31	35.36
			L-Proline in 2 $mol \cdot L^{-1}$ NaCl				
0.0000	35.70	35.47	35.26	35.07	35.00	34.95	34.91
0.1893	35.06	34.88	34.68	34.59	34.49	34.41	34.35
0.3854	34.44	34.24	34.06	33.89	33.82	33.78	33.74
0.5881	33.70	33.54	33.38	33.29	33.24	33.25	33.23
0.7988	33.04	32.91	32.81	32.72	32.72	32.68	32.69
1.0166	32.38	32.27	32.19	32.14	32.14	32.17	32.17
1.2426	31.81	31.73	31.65	31.59	31.58	31.60	31.62
1.4782	31.31	31.24	31.17	31.11	31.10	31.12	31.10
1.7234	30.78	30.69	30.66	30.59	30.58	30.60	30.61
			L-Proline in 2 $mol \cdot L^{-1}$ $NaNO_3$				
0.0000	36.22	35.97	35.85	35.80	35.72	35.64	35.61
0.1841	35.46	35.29	35.15	35.05	35.07	35.07	35.09
0.3748	34.78	34.62	34.52	34.48	34.47	34.48	34.48
0.5725	34.13	34.01	33.88	33.82	33.84	33.82	33.82
0.7773	33.50	33.38	33.28	33.22	33.21	33.23	33.25
0.9898	32.90	32.76	32.67	32.59	32.61	32.61	32.62
1.2110	32.33	32.24	32.15	32.10	32.08	32.08	32.07
1.4404	31.81	31.72	31.62	31.56	31.56	31.57	31.58
1.6789	31.31	31.20	31.15	31.08	31.07	31.08	31.10

been found to be within 0.5 $m\cdot s^{-1}$, $2.0\cdot10^{-4}$ $g\cdot cm^{-3}$, and $1.0\cdot10^{-4}$ $mol\cdot kg^{-1}$, respectively.

Results and Discussion

The measured ultrasonic velocity and density values of L-phenylalanine, L-leucine, L-glutamic acid, and L-proline + 2 $mol\cdot L^{-1}$ aqueous NaCl/2 $mol\cdot L^{-1}$ aqueous $NaNO_3$ systems as functions of molal concentration of amino acid and temperatures of (298.15, 303.15, 308.15, 313.15, 318.15, 323.15, and 328.15) K are listed in Tables 1 and 2, respectively. The density values for the systems investigated increase with an increase in molal concentration of amino acid as well as with temperature. The ultrasonic velocity values exhibit an increasing trend with an increase in the molality of amino acids in the 2 $mol\cdot L^{-1}$ aqueous NaCl and 2 $mol\cdot L^{-1}$ aqueous $NaNO_3$ solutions and in temperature in all of the systems under investigation. The increase in ultrasonic velocity values of L-phenylalanine, L-leucine, L-glutamic acid, and L-proline + 2 $mol\cdot L^{-1}$ aqueous NaCl/2 $mol\cdot L^{-1}$ aqueous $NaNO_3$ solutions may be attributed to the overall increase of cohesion brought about by the solute−solute, solute−solvent, and solvent−solvent interactions in solutions. The amino acid molecule exists as a zwitterion in neutral solution. Amino acid molecules/zwitterions may occupy the cavities of water clusters leading to the formation of denser structure of electrolyte solution.[21] Kirkwood[22] developed a theory based on electrostatic attraction between ions and zwitterions. Similar trends of variation of ultrasonic velocity with an increase in concentration of solute have been reported by other authors.[23−28] The interactions between the ions and the charged end groups of zwitterions ($-NH_3^+$, $-COO^-$) may influence the hydration cosphere of amino acids.

The isentropic compressibility[29] is given by the Newton−Laplace expression:

$$\kappa_s = 1/\rho u^2 \qquad (1)$$

The isentropic compressibility values of L-phenylalanine, L-leucine, L-glutamic acid, and L-proline in 2 $mol\cdot L^{-1}$ aqueous NaCl and 2 $mol\cdot L^{-1}$ aqueous $NaNO_3$ solutions as functions of amino acid concentration and temperature have been listed in Table 3. The κ_s values of 2 $mol\cdot L^{-1}$ aqueous NaCl and 2 $mol\cdot L^{-1}$ aqueous $NaNO_3$ solutions at 298.15 K have been found to be $35.71\cdot10^{-11}$and $36.22\cdot10^{-11}$ ($m^2\cdot N^{-1}$), respectively, whereas the corresponding literature value for water is $44.10\cdot10^{-11}$ $m^2\cdot N^{-1}$.[30] The lesser κ_s values of 2 $mol\cdot L^{-1}$ aqueous NaCl and 2 $mol\cdot L^{-1}$ aqueous $NaNO_3$ than that of water may be ascribed to (i) an introduction of incompressible Na^+, Cl^-, and NO_3^- ions into water and (ii) the changes occurring in the structure of water clusters around the ions. According to the Kirkwood model, the addition of NaCl and $NaNO_3$ into water may coordinate the hydration spheres of the sodium ions with those of the carboxylate end groups and those of chloride ions and nitrate ions with ammonium end groups of zwitterions. The ion−zwitterion interactions may cause the relaxation of water molecules to the bulk state. An increase in the amount of amino acid in a solution causes an increase in electrostriction, which in turn decreases the isentropic compressibility of solution. The κ_s values of 2 $mol\cdot L^{-1}$ aqueous solution of NaCl ($35.71\cdot10^{-11}$ $m^2\cdot N^{-1}$ at 298.15 K) and 2 $mol\cdot L^{-1}$ aqueous solution of $NaNO_3$ ($36.22\cdot10^{-11}$ $m^2\cdot N^{-1}$ at 298.15 K) are smaller than the κ_s values of 1.5 $mol\cdot L^{-1}$ aqueous solution of NaCl ($37.47\cdot10^{-11}$ $m^2\cdot N^{-1}$) and 1.5 $mol\cdot L^{-1}$ aqueous solution of $NaNO_3$ ($37.76\cdot10^{-11}$ $m^2\cdot N^{-1}$) at 298.15 K, respectively.[6] The smaller κ_s value of 2 $mol\cdot L^{-1}$ aqueous NaCl solution ($35.71\cdot10^{-11}$ $m^2\cdot N^{-1}$) than that of 2 $mol\cdot L^{-1}$ aqueous $NaNO_3$ solution ($36.22\cdot10^{-11}$ $m^2\cdot N^{-1}$) at 298.15 K is due to smaller size of Cl^- than NO_3^-.[31,32] The decrease in isentropic compressibility with an increase in temperature may be ascribed to changes occurring in the structure of water clusters around zwitterions and ions (Na^+, Cl^-, and NO_3^-).[33−36] The thermal rupture of water clusters with an increase in temperature may bring smaller aggregates of water close to each other. However, the temperature coefficient of isentropic compressibility of pure water becomes zero at 64 °C.[37] The peculiar structure of water seems to be responsible for this anomalous behavior.[35]

Conclusions

The ultrasonic velocity values of L-phenylalanine, L-leucine, L-glutamic acid, and L-proline + 2 $mol\cdot L^{-1}$ aqueous NaCl and 2 $mol\cdot L^{-1}$ aqueous $NaNO_3$ solutions increase with an increase in the molality of the amino acid as well as temperature from T = (298.15 to 328.15) K. The density values increase with an increase in the molality of the amino acid and decrease with an increase in temperature for the systems under investigation. The isentropic compressibilities decrease with an increase in the molal concentration of the amino acid as well as temperature.

Acknowledgment

The authors are thankful to the Chairman Department of Chemistry, A. M. U. Aligarh, for providing the necessary facility for the compilation of this work.

Literature Cited

(1) Pilani, R.; Saravanan, S. Volumetric, Compressibility and Transport Studies of Some Amino Acids in Aqueous Magnesium Acetate at 298.15 K. *Res. J. Phys.* **2008**, *2*, 13–21.
(2) Badarayani, R.; Kumar, A. Effect of Temperature on Volumetric Properties of L-alanine(1) + KCl(2) + H_2O(3) system. *J. Chem. Eng. Data* **2003**, *48*, 664–668.
(3) Wadi, R. K.; Goyal, R. K. Temperature Dependence of Apparent Molal Volumes and Viscosity B-Coefficients of Amino Acids in Aqueous Potassium Thiocyanate Solutions from 15 to 35 °C. *J. Solution Chem.* **1992**, *2*, 163–170.
(4) Banipal, T. S.; Damanjit, K.; Banipal, P. K. Apparent Molar Volumes and Viscosities of Some Amino Acids in Aqueous Sodium Acetate Solutions at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 1236–1246.
(5) Singh, S. K.; Kishore, N. Partial Molar Volumes of Amino Acids and Peptides in Aqueous Salt Solutions at 25 °C and a Correlation with Stability of Proteins in the Presence of Salts. *J. Solution Chem.* **2003**, *2*, 163–170.
(6) Riyazuddeen; Bansal, G. K. Intermolecular/Interionic Interactions in L-Leucine, L-Asparagine and Glycylglycine-Aqueous Electrolyte Systems. *Thermochim. Acta* **2006**, *445*, 40–48.
(7) Riyazuddeen; Basharat, R. Intermolecular/Interionic Interactions in L-Isoleucine, L-Proline, L-Glutamine-Aqueous Electrolyte Systems. *J. Chem. Thermodyn.* **2006**, *38*, 1684–1695.
(8) Riyazuddeen; Khan, I. Interactions in L-Alanine/L-Proline/L-Valine/L-Leucine-Aqueous KCl/KNO_3 Systems at Different Temperatures: An Isentropic Compressibility Study. *Thermochim. Acta* **2008**, *483*, 45–48.
(9) Riyazuddeen; Khan, I. Effect of KCl and KNO_3 on Partial Molal Volumes and Partial Molal Compressibility of Some Amino Acids at Different Temperatures. *Int. J. Thermophys.* **2009**, *30*, 475–489.
(10) Riyazuddeen; Khan, I. Viscosity Studies of L-Alanine, L-Proline, L-Valine, L-Leucine + Aqueous KCl/KNO_3 Solutions at Different Temperatures. *J. Chem. Thermodyn.* **2008**, *40*, 1549–1551.
(11) Riyazuddeen; Altamash, T. Ultrasonic Velocities and Densities of L-Histidine or L-Glutamic Acid or L-Tryptophan or Glycylglycine + 2mol$\cdot L^{-1}$ Aqueous KCl or KNO_3 Solutions from (298.15 to 323.15) K. *J. Chem. Eng. Data* **2009**, *54*, 3133–3139.
(12) Sadeghi, R.; Parhizkar, H. Volumetric, Isentropic Compressibility and Electrical Conductivity of Solutions of Tri-sodium Phosphate in 1-propanol + water Mixed-solvent Media over the Temperature Range of 283.15−303.15 K. *Fluid Phase Equilib.* **2008**, *265*, 173–183.
(13) Hasan, M.; Shirude, D. F.; Hiray, A. P.; Kadam, U. P.; Sawant, A. B. Densities, Viscosities and Ultrasonic Velocity Studies of Binary Mixtures of Toluene with Heptan-1-ol, Octan-1-ol and Decan-1-ol at 298.15 and 308.15 K. *J. Mol. Liq.* **2007**, *135*, 32–37.

(14) Dhondge, S. S.; Pandhurnekar, C.; Ramesh, L. Thermodynamic Studies of Some Non-electrolytes in Aqueous Solutions at Low Temperatures. *J. Chem. Thermodyn.* **2008**, *40*, 1–15.

(15) Ali, A.; Nabi, F. Intermolecular Interactions in Binary Liquid Mixtures of Styrene with *m*-, *o*-, or *p*-xylene. *Acta Phys. Chim. Sin.* **2008**, *24*, 47–54.

(16) Ali, A.; Tariq, M.; Patel, R.; Ittoo, F. A. Interaction of Glycine with Cationic, Anionic, and Nonionic Surfactants at Different Temperatures: a Volumetric, Viscometric, Refractive Index, Conductometric, and Fluorescence Probe Study. *Colloid Polym. Sci.* **2008**, *286*, 183–190.

(17) Islam, S.; Waris, B. N. Intermolecular/Interionic interactions in Leucine-, NaCl-, and KCl- Aqueous Urea Systems. *Thermochim. Acta* **2004**, *424*, 165–174.

(18) Riyazuddeen; Islam, N. Ultrasonic Velocities and Molecular Interactions in Ternary Mixtures of Amino Acids in Aqueous Medium. *J. Pure Appl. Ultrasonics* **1997**, *19*, 16–25.

(19) Kell, G. S. Density, Thermal Expansivity and Compressibility of Liquid Water from 0 °C to 150 °C, Correlations and Table for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale. *J. Chem. Eng. Data* **1975**, *20*, 97–105.

(20) Del Grosso, V. A.; Mader, C. W. Speed of Sound in Pure Water. *J. Acoust. Soc. Am.* **1972**, *52*, 1442–1446.

(21) Rao, N. P.; Verrall, R. E. Ultrasonic Velocity, Excess Adiabatic Compressibility, Apparent Molar Volume and Apparent Molar Compressibility Properties of Binary Liquids Mixture Containing 2-But Oxyethanol. *Can. J. Chem.* **1987**, *65*, 810–816.

(22) Kirkwood, J. G. Theory of Solutions of Molecules Containing Widely Separated Charges with Special Application to Zwitterions. *J. Chem. Phys.* **1934**, *2*, 351–361.

(23) Hirata, F.; Arakawa, K. Ultrasonic Study of Solute-Solvent Interactions in Aqueous Solutions of Tetraalkylammonium Salts. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2715–2719.

(24) Magazu, S.; Migliardo, P.; Musolino, A. M.; Sciortino, M. T. α,α-Terehalose-Water Solutions. 1. Hydration Phenomena and Anomalies in the Acoustic Properties. *J. Phys. Chem. B* **1997**, *101*, 2348–2351.

(25) Rohman, N.; Mohiuddin, S. Concentration and Temperature Dependence of Ultrasonic Velocity and Isentropic Compressibility in Aqueous Sodium Nitrate and Sodium Thiosulphate Solutions. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2053–2056.

(26) Ragouramane, D.; Rao, A. S. Ultrasonic Studies on the Influence of Some Amino Acids on Molecular Interactions in Aqueous Solutions of Ethanol. *Indian J. Chem.* **1998**, *37A*, 659–662.

(27) Badarayani, R.; Kumar, A. Density and Speed of Sound of Glycine in Concentrated Aqueous NaBr, KCl, KBr and $MgCl_2$ at $T = 298.15$ K. *J. Chem. Thermodyn.* **2003**, *35*, 897–908.

(28) Thirumaran, S.; Sabu, K. J. Ultrasonic Investigation of Amino Acids in Aqueous Sodium Acetate Medium. *Indian J. Pure Appl. Phys.* **2009**, *47*, 87–96.

(29) Chalikian, T. V.; Sarvazyan, A. P.; Funk, T.; Cain, C. A.; Breslauer, K. J. Partial Molar Characteristics of Glycine and Alanine in Aqueous Solutions at High Pressures Calculated from Ultrasonic Velocity Data. *J. Phys. Chem.* **1994**, *98*, 321–328.

(30) Mendonca, A. F. S. S.; Dias, S. M. A.; Dias, F. A.; Barata, B. A. S.; Lampreia, I. M. S. Temperature Dependence of Thermodynamic Properties of Leucyl-glycine Aqueous Solutions from 15 to 45 °C. *Fluid Phase Equilib.* **2003**, *212*, 67–79.

(31) Blandamer, M. J.; Symons, M. C. R. Significance of New Values for Ionic Radii to Solvation Phenomenon in Aqueous Solution. *J. Phys. Chem.* **1963**, *67*, 1304–1306.

(32) Masterton, W. L.; Bolocofsk, D.; Lee, T. P. Ionic Radii From Scaled Particle Theory of The Salt Effect. *J. Phys. Chem.* **1971**, *75*, 2809–2815.

(33) Millero, F. J.; Surdo, A. L.; Shin, C. The Apparent Molal Volume and Adiabatic Compressibility of Aqueous Amino Acids at 25 °C. *J. Phys. Chem.* **1978**, *82*, 784–792.

(34) Millero, F. J.; Lepple, F. K. Isothermal Compressibility of Deuterium Oxide at Various Temperatures. *J. Chem. Phys.* **1971**, *54*, 946–949.

(35) Hall, L. The Origin of Ultrasonic Absorption in Water. *Phys. Rev.* **1948**, *73*, 775–781.

(36) Feates, F. S.; Ives, D. J. G. The Ionization Functions of Cyanoacetic Acid in Relation to the Structure of Water and the Hydration of Ions and Molecules. *J. Chem. Soc.* **1956**, 2798–2812.

(37) Uedaira, H.; Suzuki, Y. Ultrasonic Velocity and Compressibility in Aqueous Solutions of Alkali Metal Chlorides. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2787–2790.

Received for review October 29, 2009. Accepted March 15, 2010. One of the authors (S.A.) wishes to acknowledge to UGC for granting the Research Fellowship.

JE900909S