JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Densities, Speeds of Sound, and Viscosities of (L-Proline + Aqueous Glucose) and (L-Proline + Aqueous Sucrose) Solutions in the Temperature Range (298.15 to 323.15) K

Riyazuddeen* and Mohd Amil Usmani

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

S *Supporting Information*

ABSTRACT: Densities (ρ), speeds of sound (u), and viscosities (η) of L-proline in 1 $\text{mol}\cdot\text{L}^{-1}$ aqueous glucose/1 $\text{mol}\cdot\text{L}^{-1}$ aqueous sucrose solutions have been measured as a function of molal concentration of L-proline at temperatures of (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K. Using the ρ and u data, the partial molar volumes (ϕ_v^o), transfer partial molar volumes ($\Delta_{tr}\phi_v^o$), isentropic compressibilities (κ_s), partial molar isentropic compressibilities (ϕ_k^o), and transfer partial molar isentropic compressibilities ($\Delta_{tr}\phi_k^o$) have been computed. The viscosity *B*-coefficients of the Jones–Dole equation also have been computed. The κ_s values decrease with increase in molal concentration of L-proline and also with increase in temperature. The ϕ_v^o increase and ϕ_k^o decrease with an increase in temperature. The $\Delta_{tr}\phi_v^o$ values increase and $\Delta_{tr}\phi_k^o$ values decrease with an increase in temperature. The trends of variations of experimental and computed parameters have been discussed in terms of hydrophilic–ionic group and hydrophilic–hydrophobic interactions operative in the systems.

INTRODUCTION

Sugars help in stabilizing the native confirmation of globular proteins and enzymes.[1−4] However, the understanding of the mechanism of stabilization of proteins by sugars is still incomplete. One approach that may help in understanding about the nature of protein–sugar interactions and requires less complex measurement techniques is to study the amino acid–sugar interactions in solutions. L-Proline is the only native amino acid that has a pyrrole ring. The cyclic structure diminishes the interactions between the L-proline molecules due to the steric effect, which makes hydration easier. At the same time, its relatively large nonpolar group makes hydrophobic interactions predominant. L-Proline as a special amino acid draws more attention to deepen the understanding of solute–solvent interactions.[5]

Nain et al. have studied the volumetric, ultrasonic, and viscometric behavior of L-histidine in aqueous glucose solutions.[6] Pal et al. have studied the density, viscosity, and speed of sound of diglycine in aqueous xylose, L(-)arabinose, and D(-)ribose solutions;[7] in aqueous glucose, galactose, and fructose solutions;[8] of L-alanine in aqueous fructose, maltose, and lactose solutions;[9] and the density of L-alanine and L-valine in aqueous sucrose solutions.[10] Palani and Geetha have studied the density, viscosity, and ultrasonic velocity of L-serine, L-glutamine, and L-asparagine in aqueous glucose solutions.[11] Ali et al. have studied the density, viscosity, and refractive index of glycine, DL-alanine, L-serine, and DL-valine in aqueous glucose solution.[12] Li et al. have studied the density of glycine, L-alanine, and L-serine in aqueous glucose solutions.[13] Zhao et al. have studied the density and viscosity of arginine in aqueous glucose and sucrose solutions.[14] Banipal et al. have studied the speed of sound of glycine, DL-alanine, diglycine, and triglycine in aqueous solution of glucose.[15]

To understand the nature of interactions of sugars with amino acids in aqueous solutions, the values of density (ρ), speed of sound (u), and viscosity (η) of L-proline in 1 $\text{mol}\cdot\text{L}^{-1}$ aqueous glucose and 1 $\text{mol}\cdot\text{L}^{-1}$ aqueous sucrose solutions as a function of molal concentrations of L-proline at temperatures: (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K have been measured. Using the experimentally measured ρ, u and η data, the partial molar volumes (ϕ_v^o), transfer partial molar volumes ($\Delta_{tr}\phi_v^o$), isentropic compressibilities (κ_s), partial molar isentropic compressibilities (ϕ_k^o), transfer partial molar isentropic compressibilities ($\Delta_{tr}\phi_k^o$), and viscosity *B*-coefficients of the Jones–Dole equation for L-proline in 1 $\text{mol}\cdot\text{L}^{-1}$ aqueous glucose and 1 $\text{mol}\cdot\text{L}^{-1}$ aqueous sucrose solutions have been evaluated. Among various physical parameters, these thermodynamic parameters have been recognized as being sensitive to structural changes occurring in solutions. The measured and computed parameters have been discussed in terms of hydrophilic–ionic group and hydrophilic–hydrophobic interactions occurring in the solutions.

MATERIALS AND METHODS

The L-proline and the sugars: glucose and sucrose of high purity (mass fraction ≥ 99 %), used in the present studies, were purchased from SRL (India) and E. Merck (India), respectively. The L-proline was 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. The glucose and sucrose 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 1 $\text{mol}\cdot\text{L}^{-1}$ aqueous glucose and 1 $\text{mol}\cdot\text{L}^{-1}$ aqueous sucrose were prepared at 298.15 K in triply distilled

Received: January 8, 2011
Accepted: July 13, 2011
Published: July 28, 2011

dx.doi.org/10.1021/je2000205 | *J. Chem. Eng. Data* 2011, 56, 3504–3509

Table 1. Densities ($\rho/10^{-3}$ kg·m^{-3}) as Functions of Molal Concentration of L-Proline in 1.13 mol·kg^{-1} Aqueous Glucose/1.27 mol·kg^{-1} Aqueous Sucrose Solution and Temperature

m	T/K					
mol·kg^{-1}	298.15	303.15	308.15	313.15	318.15	323.15
	L-Proline in Aqueous Glucose Solution					
0.0000	1.065068	1.063297	1.061359	1.059245	1.056983	1.054253
0.1912	1.069914	1.068091	1.066123	1.063981	1.061671	1.058923
0.3893	1.074682	1.072853	1.070831	1.068662	1.066343	1.063582
0.5947	1.079392	1.077613	1.075582	1.073410	1.070982	1.068224
0.8079	1.084234	1.082324	1.080242	1.078042	1.075553	1.072892
1.0296	1.088891	1.087082	1.084851	1.082614	1.080163	1.077534
1.2601	1.093633	1.091614	1.089381	1.087144	1.084652	1.082052
1.5002	1.098472	1.096324	1.094124	1.091763	1.089353	1.086691
	L-Proline in Aqueous Sucrose Solution					
0.0000	1.127374	1.125373	1.123197	1.120735	1.118184	1.115445
0.1805	1.130924	1.128832	1.126630	1.124123	1.121551	1.118823
0.3676	1.134381	1.132272	1.129954	1.127432	1.124872	1.122171
0.5615	1.137872	1.135614	1.133282	1.130791	1.128163	1.125424
0.7625	1.141343	1.139080	1.136683	1.134062	1.131504	1.128783
0.9716	1.144890	1.142391	1.139900	1.137314	1.134632	1.131962
1.1888	1.148242	1.145673	1.143334	1.140473	1.137814	1.135233
1.4153	1.151714	1.148972	1.146520	1.143824	1.140823	1.138324

Table 2. Speeds of Sound (u/m·s^{-1}) as Functions of Molal Concentration of L-Proline in 1.13 mol·kg^{-1} Aqueous Glucose/1.27 mol·kg^{-1} Aqueous Sucrose Solution and Temperature

m	T/K					
mol·kg^{-1}	298.15	303.15	308.15	313.15	318.15	323.15
	L-Proline in Aqueous Glucose Solution					
0.0000	1564.80	1574.30	1582.38	1589.06	1594.42	1598.53
0.1912	1577.84	1586.70	1594.19	1600.35	1605.25	1608.94
0.3893	1590.99	1599.25	1606.20	1611.86	1616.29	1619.55
0.5947	1604.19	1611.87	1618.30	1623.47	1627.45	1630.30
0.8079	1615.98	1623.13	1628.95	1633.61	1637.11	1639.51
1.0296	1627.62	1634.16	1639.51	1643.68	1646.74	1648.72
1.2601	1639.14	1645.08	1649.90	1653.59	1656.19	1657.76
1.5002	1650.44	1655.85	1660.16	1663.38	1665.55	1667.71
	L-Proline in Aqueous Sucrose Solution					
0.0000	1607.89	1615.56	1621.92	1627.00	1630.84	1633.30
0.1805	1621.95	1628.92	1634.68	1639.20	1642.54	1644.75
0.3676	1635.24	1641.62	1646.79	1650.89	1653.63	1655.40
0.5615	1648.01	1653.79	1658.40	1661.70	1664.06	1665.36
0.7625	1660.27	1665.43	1669.47	1672.42	1674.30	1675.17
0.9716	1671.90	1676.53	1680.07	1682.56	1684.02	1684.52
1.1888	1683.80	1687.87	1690.90	1692.92	1693.96	1694.08
1.4153	1694.21	1697.78	1700.35	1701.93	1702.55	1702.96

water and were used as solvents for the preparation of L-proline solutions. All of the solutions were prepared by Mettler Toledo balance with a precision of ± 0.0001 g. The molalities of 1 mol·L^{-1} aqueous glucose and 1 mol·L^{-1} aqueous sucrose solutions were found to be 1.13 mol·kg^{-1} and 1.27 mol·kg^{-1}, respectively. The specific conductance of triply distilled water used was less than $1.1\cdot10^{-6}$ Ω^{-1}·cm^{-1}. All of the solutions were stored in special airtight bottles to avoid the exposure of solutions to air and evaporation. Densities and speeds of sound of L-proline in 1 mol·L^{-1} aqueous glucose and 1 mol·L^{-1} aqueous sucrose were measured simultaneously using an Anton Paar DSA 5000 M instrument. Before each series of measurements, the instrument was calibrated at (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K with the triply distilled water and dry air. The uncertainties in density and speed of sound measurements were $\pm\,5\cdot10^{-3}$ kg·m^{-3} and ± 0.5 m·s^{-1}, respectively. The viscosity measurements were carried out using a suspended Ubbelohde type viscometer, which was calibrated with triply distilled water at six temperatures between (298.15 and 323.15) K. A thoroughly cleaned and perfectly dried viscometer filled with the test solution was placed vertically in the glasswalled thermostat maintained at a desired temperature (± 0.01 K). After the attainment of thermal equilibrium, efflux times of flow were recorded with an electronic watch with the resolution of 0.01 s. The average of at least four readings reproducible within 0.1 s was used as the final efflux time. The viscosity values of water at different temperatures were taken from the literature for calibration purposes.[16] The uncertainty in the measurement of viscosity was $\pm\,3\cdot10^{-6}$ N·m^{-2}·s.

■ RESULTS AND DISCUSSION

The experimentally measured density and speed of sound values of L-proline in 1 mol·L^{-1} aqueous glucose and 1 mol·L^{-1} aqueous sucrose solutions as functions of molal concentration of L-proline and temperature: (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K, have been listed in Tables 1 and 2, respectively.

Partial Molar Volume and Transfer Partial Molar Volume. The apparent molar volumes ϕ_v of L-proline have been calculated from the density values of solvent and solution using the relation,

$$\phi_v = (M/\rho) - \{(\rho - \rho_o)/m\rho\rho_o\} \tag{1}$$

where m is the molality (mol·kg^{-1}) of the solution, M is the molar mass of the solute (L-proline) (kg·mol^{-1}), and ρ_o and ρ are the density values of the solvent and solution, respectively. The apparent molar volume values have been fitted by employing the least-squares method to the linear equation,

$$\phi_v = \phi_v^o + S_v m \tag{2}$$

where ϕ_v^o is partial molar volume of the solute and S_v is the volumetric pairwise interaction coefficient.[17,18] The ϕ_v^o, S_v, and standard deviation (σ_v) values are presented in Table 3. A comparison of observed and literature values of ϕ_v^o has been given in Table S1 of the Supporting Information. The ϕ_v^o of L-proline in 1 mol·L^{-1} aqueous glucose and 1 mol·L^{-1} aqueous sucrose solutions have been found to be higher than those in aqueous solution. These results can be explained by the cosphere overlap model developed by Gurney[19] and Frank and Evans.[20] The interactions occurring between L-proline and 1 mol·L^{-1} aqueous glucose/1 mol·L^{-1} aqueous sucrose solution can be classified as follows:[21−24]

(i) Hydrophilic−ionic interactions between the OH groups of the glucose/sucrose molecules and zwitterionic center of L-proline.

Table 3. ϕ_v^o, S_v, and σ_v at Different Temperatures

T	$\phi_v^o \cdot 10^6$	$S_v \cdot 10^6$	$\sigma_v \cdot 10^6$
K	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-2} \cdot kg$	$m^3 \cdot mol^{-1}$
	L-Proline in Aqueous Glucose Solution		
298.15	85.45 ± 0.06	0.273 ± 0.067	0.07
303.15	85.66 ± 0.03	0.314 ± 0.034	0.04
308.15	85.92 ± 0.04	0.365 ± 0.046	0.05
313.15	86.16 ± 0.04	0.376 ± 0.041	0.05
318.15	86.54 ± 0.03	0.316 ± 0.037	0.04
323.15	86.80 ± 0.02	0.179 ± 0.022	0.03
	L-Proline in Aqueous Sucrose Solution		
298.15	86.65 ± 0.05	0.201 ± 0.052	0.05
303.15	86.86 ± 0.03	0.318 ± 0.038	0.04
308.15	87.09 ± 0.04	0.231 ± 0.049	0.05
313.15	87.32 ± 0,04	0.323 ± 0.048	0.05
318.15	87.69 ± 0.04	0.455 ± 0.048	0.05
323.15	87.87 ± 0.04	0.373 ± 0.044	0.04

(ii) Hydrophilic—hydrophobic interactions between the OH groups of the glucose/sucrose molecules and the non-polar pyrrole ring of the L-proline.

The electrostriction at zwitterionic terminals due to ionic—hydrophilic interactions between the zwitterionic center of L-proline and the —OH group of glucose/sucrose molecules decrease, which in turn, cause the larger values of ϕ_v^o of L-proline in 1 $mol \cdot L^{-1}$ aqueous glucose/aqueous sucrose solutions than in pure water. The large values of ϕ_v^o of L-proline in 1 $mol \cdot L^{-1}$ aqueous sucrose solution than in 1 $mol \cdot L^{-1}$ aqueous glucose solution is due to the strong hydrophilic—ionic interactions in aqueous sucrose solution as a sucrose molecule contains a larger number of —OH groups than a glucose molecule. The increase in ϕ_v^o values of L-proline with an increase in temperature between (298.15 and 323.15) K in 1 $mol \cdot L^{-1}$ aqueous glucose or 1 $mol \cdot L^{-1}$ sucrose solution can be explained by considering the size of primary and secondary solvation layers around the zwitterions of L-proline. The water molecule from the secondary solvation layer of L-proline zwitterions is released into the bulk of the water, which results in the larger ϕ_v^o values of L-proline in 1 $mol \cdot L^{-1}$ aqueous glucose/sucrose solutions at higher temperatures.[6,25,26] The S_v values for L-proline are found to be positive but smaller than ϕ_v^o values, suggesting that solute—solute interactions are weaker than solute—solvent interactions in the systems under study. A similar type of interactions has been also reported by Huaji et al.,[27] in their enthalpic studies of glycine, alanine, and serine in aqueous sorbose and fructose at T = 298.15 K.

The partial molar volume of transfer of L-proline from water to 1 $mol \cdot L^{-1}$ aqueous glucose/sucrose solution at the temperature ($\Delta_{tr}\phi_v^o$) is defined as,

$$\Delta_{tr}\phi_v^o = \phi_{v(\text{aqueous glucose/aqueous sucrose})}^o - \phi_{v(\text{water})}^o \qquad (3)$$

The $\Delta_{tr}\phi_v^o$ values of L-proline in 1 $mol \cdot L^{-1}$ aqueous glucose and 1 $mol \cdot L^{-1}$ aqueous sucrose solutions have been reported in Table S2 of the Supporting Information. Interactions of type (i) lead to a positive contribution to $\Delta_{tr}\phi_v^o$, since owing to the overlap of the hydration cosphere of an ion (NH_3^+ and COO^- groups) and a hydrophilic OH group, the structure-braking tendency of the ion and the electrostrition of the solvent caused by these ions are reduced. On the contrary, interactions of type (ii), between the OH groups of glucose/sucrose and nonpolar pyrrole of L-proline, should lead to a decrease in $\Delta_{tr}\phi_v^o$ values because of the reduction of water structure that is formed around the groups as a result of their cosphere overlap. Thus, the ionic—hydrophilic interactions dominate over the hydrophilic—hydrophobic interactions of L-proline in 1 $mol \cdot L^{-1}$ aqueous glucose and 1 $mol \cdot L^{-1}$ aqueous sucrose solutions. The $\Delta_{tr}\phi_v^o$ values of L-proline in 1 $mol \cdot L^{-1}$ aqueous sucrose solution is found to be higher than those in 1 $mol \cdot L^{-1}$ aqueous glucose solution. This further reinforces the contention that the ionic—hydrophilic interactions between $NH_3^+$and COO^- groups of L-proline zwitterion and OH groups of sucrose molecules are stronger than those with glucose molecules. The decrease in $\Delta_{tr}\phi_v^o$ values with increase in temperature indicates the corresponding decrease in number of electrostricted water molecules in the solution. The similar trends of variations of ϕ_v^o and $\Delta_{tr}\phi_v^o$ were also observed by Nain et al.[6] and other workers.[7−10,28]

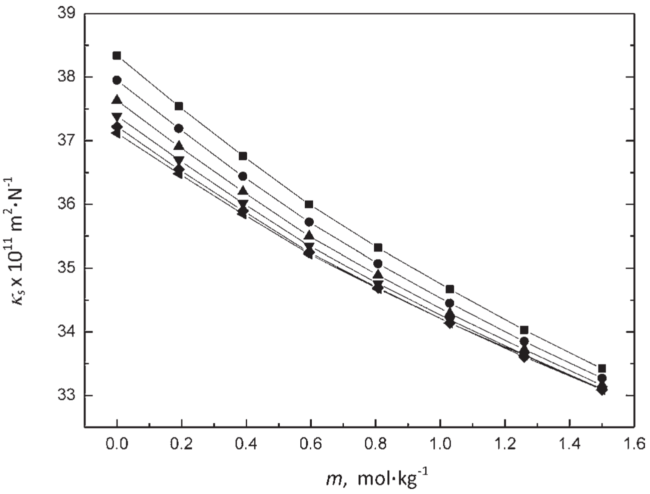

Figure 1. κ_s versus molality of L-proline in aqueous glucose solution. ■, T = 298.15 K; ●, T = 303.15 K; ▲, T = 308.15 K; ▼, T = 313.15 K; ◆, T = 318.15 K; left-pointing triangle, T = 323.15 K.

Isentropic Compressibility. The isentropic compressibility values have been calculated using the following Newton—Laplace relation:

$$\kappa_s = \frac{1}{\rho u^2} \qquad (4)$$

The isentropic compressibility values of L-proline in 1 $mol \cdot L^{-1}$ aqueous glucose and 1 $mol \cdot L^{-1}$ aqueous sucrose solutions as a function of molality of L-proline at different temperatures have been plotted in the Figures 1 and 2. The isentropic compressibility values decrease with an increase in the molal concentration of L-proline as well as with an increase in temperature. The decrease in κ_s values of 1 $mol \cdot L^{-1}$ aqueous glucose/sucrose solution on the introduction of the amount of L-proline into solutions indicates that the water molecules around L-proline molecule are less compressible than the water molecules in the bulk solution.[29,30] The decrease in isentropic compressibilities of solutions may be due to (i) the introduction of L-proline molecules into solution which reduces the cavities in solution, (ii) the increase in hydrophilic—ionic interactions, and (iii) increase in hydrophilic—hydrophobic interactions. The κ_s values of 1 $mol \cdot L^{-1}$ aqueous glucose and 1 $mol \cdot L^{-1}$ aqueous sucrose

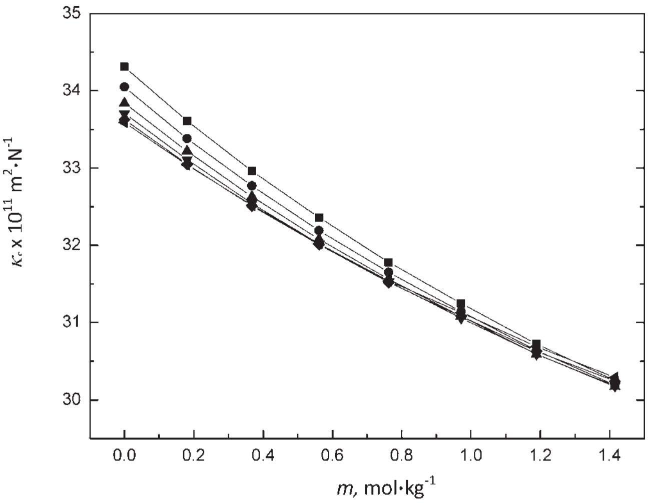

Figure 2. κ_s versus molality of L-proline in aqueous sucrose solution. ■, $T = 298.15$ K; ●, $T = 303.15$ K; ▲, $T = 308.15$ K; ▼, $T = 313.15$ K; ◆, $T = 318.15$ K; left-pointing triangle, $T = 323.15$ K.

solutions at 298.15 K have been found to be $38.34 \cdot 10^{-11}$ $m^2 \cdot N^{-1}$ and $34.31 \cdot 10^{-11}$ $m^2 \cdot N^{-1}$, respectively, whereas the corresponding reported value of water is $44.77 \cdot 10^{-11}$ $m^2 \cdot N^{-1}$.[31] The lesser κ_s values of 1 M aqueous glucose and 1 M aqueous sucrose solutions than that of pure water may be ascribed to the formation of less compressible first hydration shell of glucose and sucrose molecules than the bulk water.[32] The lesser κ_s value of 1 mol·L^{-1} aqueous sucrose ($34.31 \cdot 10^{-11}$, $m^2 \cdot N^{-1}$ at 298.15 K) than that of 1 mol·L^{-1} aqueous glucose solution ($38.34 \cdot 10^{-11}$, $m^2 \cdot N^{-1}$ at 298.15 K) at all temperatures of study suggests the presence of stronger hydrophilic—ionic interactions in 1 mol·L^{-1} aqueous sucrose solution than those in 1 mol·L^{-1} aqueous glucose solution.[33] The decrease in isentropic compressibility with an increase in temperature may be ascribed to changes occurring in the hydrogen bonded structure of water clusters around L-proline zwitterions and hydrophilic groups of glucose/sucrose molecules. The thermal rupture of water clusters with an increase in temperature may bring smaller aggregates of water molecules close to each other, leading to higher κ_s values.

Partial Molar Isentropic Compressibility and Transfer Partial Molar Isentropic Compressibility. The apparent molar isentropic compressibilities, ϕ_k, have been calculated using the relation,

$$\phi_k = \{(\kappa_s - \kappa_o)/m\rho_o\} + \kappa_s \phi_v \tag{5}$$

In the above equation, m is the molality of the solution (mol·kg^{-1}), ρ_o is the density of the solvent (kg·m^{-3}), and κ_s ($= 1/\rho u^2$) and κ_o ($= 1/\rho_o\, u_0^2$) are the isentropic compressibilities of the solution and solvent ($m^2 \cdot N^{-1}$), respectively. The ϕ_k values have been fitted by the least-squares method with the equation,

$$\phi_k = \phi_k^o + S_k m \tag{6}$$

where ϕ_k^o is the apparent molar isentropic compressibility at infinite dilution, which is also referred to as the partial molar isentropic compressibility, and is a measure of solute—solvent interactions. The computed ϕ_k^o, S_k, and σ_k (standard deviation) values have been listed in the Table 4. The comparison between observed and literature values of ϕ_k^o have been given in Table S1 of the Supporting Infomation. The partial molar isentropic compressibilities of L-proline in 1 mol·L^{-1} aqueous glucose and 1 mol·L^{-1} aqueous sucrose solutions are higher than the corresponding values of aqueous systems. The ϕ_k^o values of L-proline in 1 mol·L^{-1} aqueous glucose and 1 mol·L^{-1} aqueous sucrose solutions increase with an increase in temperature. The ϕ_k^o values of all of the systems are negative at all temperatures of study except in 1 mol·L^{-1} aqueous sucrose at 323.15 K. The negative values of ϕ_k^o suggest that water molecules around ionic charged groups of zwitterions are less compressible than the water molecules in the bulk solution,[28,29] and a slightly positive value indicates the lesser electrostriction of water molecule around the zwitterion at 323.15 K. The increase in ϕ_k^o values with the increase in temperature indicates the release of water molecules from the secondary solvation layer of L-proline zwitterions into the bulk which make the solutions more compressible.[21,22] The positive values of S_k for L-proline in 1 mol·L^{-1} aqueous glucose/sucrose solutions indicate the existence of weak solute—solute interactions in these systems. This observation further supports the conclusion that the hydrophilic—ionic groups interactions dominate in these systems.

Table 4. ϕ_k^o, S_k, and σ_k at Different Temperatures

T	$\phi_k^o \cdot 10^{15}$	$S_k \cdot 10^{15}$	$\sigma_k \cdot 10^{15}$
K	$Pa^{-1} \cdot m^3 \cdot mol^{-1}$	$Pa^{-1} \cdot m^3 \cdot mol^{-2} \cdot kg$	$Pa^{-1} \cdot m^3 \cdot mol^{-1}$
	L-Proline in Aqueous Glucose Solution		
298.15	-8.45 ± 0.04	4.36 ± 0.21	0.25
303.15	-6.96 ± 0.03	4.28 ± 0.15	0.18
308.15	-5.42 ± 0.04	4.14 ± 0.19	0.23
313.15	-4.02 ± 0.04	3.96 ± 0.21	0.25
318.15	-2.75 ± 0.04	3.78 ± 0.25	0.29
323.15	-1.36 ± 0.05	3.29 ± 0.26	0.31
	L-Proline in Aqueous Sucrose Solution		
298.15	-5.83 ± 0.04	4.86 ± 0.27	0.31
303.15	-4.33 ± 0.03	4.76 ± 0.31	0.34
308.15	-2.18 ± 0.01	3.99 ± 0.15	0.16
313.15	-1.20 ± 0.02	4.03 ± 0.22	0.24
318.15	-0.15 ± 0.02	3.97 ± 0.21	0.23
323.15	1.23 ± 0.01	3.37 ± 0.14	0.15

Partial molar isentropic compressibilities of transfer ($\Delta_{tr}\phi_k^o$) from water to 1 mol·L^{-1} aqueous glucose or 1 mol·L^{-1} aqueous sucrose solution have been calculated using the following expression

$$\Delta_{tr}\phi_k^o = \phi_k^o(\text{aqueous glucose/aqueous sucrose}) - \phi_k^o(\text{water}) \tag{7}$$

The computed $\Delta_{tr}\phi_k^o$ values have been listed in Table S2 of the Supporting Information. The positive $\Delta_{tr}\phi_k^o$ values indicate the release of water molecules from the secondary solvation layer of L-proline zwitterions into the bulk. The release of water molecules indicates the domination of hydrophilic—ionic interactions in the (L-proline + 1 mol·L^{-1} aqueous glucose/sucrose) systems. The decrease in $\Delta_{tr}\phi_k^o$ values with an increase in temperature indicates the release of a smaller amount of water molecules from the secondary solvation layer of L-proline zwitterions into the bulk at higher temperatures.

Viscosity *B*-Coefficient. The measured viscosity values of L-proline in 1 mol·L^{-1} aqueous glucose/1 mol·L^{-1} aqueous

Table 5. Viscosities (η/10^{-4}, N·m^{-2}·s) as Functions of Molal Concentration of L-Proline in 1.13 mol·kg^{-1} Aqueous Glucose/1.27 mol·kg^{-1} Aqueous Sucrose Solution and Temperature

m	T/K					
mol·kg^{-1}	298.15	303.15	308.15	313.15	318.15	323.15
L-Proline in Aqueous Glucose Solution						
0.0000	14.890	12.777	11.472	9.944	9.095	8.291
0.1912	15.016	12.844	11.595	10.215	9.329	8.372
0.3893	16.078	14.036	12.620	10.949	10.005	9.013
0.5947	17.569	15.295	13.806	11.825	10.963	9.803
0.8079	19.141	16.662	14.930	13.048	11.688	10.539
1.0296	20.910	18.046	16.068	13.938	12.563	11.295
1.2601	22.604	19.493	17.469	15.088	13.801	12.288
1.5002	24.225	21.246	18.942	16.246	14.548	13.136
L-Proline in Aqueous Sucrose Solution						
0.0000	27.164	23.757	20.748	17.948	15.870	13.940
0.1805	27.919	25.038	21.944	19.157	17.022	15.042
0.3676	31.547	27.930	24.123	20.979	18.695	16.652
0.5615	34.361	30.031	26.373	22.509	19.686	17.418
0.7625	37.024	32.367	28.842	24.739	21.375	19.294
0.9716	40.552	34.839	30.849	26.259	23.068	20.493
1.1888	43.327	37.873	32.733	27.987	24.205	21.583
1.4153	46.589	40.894	35.865	30.740	27.170	23.373

sucrose systems as functions of molal concentration L-proline concentration and temperatures: (298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K are listed in Table 5. The viscosity of 1 mol·L^{-1} aqueous glucose solution (14.890·10^{-4} N·m^{-2}·s) is smaller than the value of 1 mol·L^{-1} aqueous sucrose (27.164·10^{-4} N·m^{-2}·s) at T = 298.15 K. The measured viscosity of 1 mol·L^{-1} aqueous glucose solution is in close agreement with the reported value (14.230·10^{-4} N·m^{-2}·s) of 0.90760 M glucose by Banipal et al.[34] at 298.15 K. The viscosity values of the systems studied (L-proline + 1 mol·L^{-1} aqueous glucose/1 mol·L^{-1} aqueous sucrose) show an increasing trend with an increasing molal concentration of L-proline in solution. This trend of variation of η values may be attributed to an increase in the hydrophilic–ionic and hydrophilic–hydrophobic interactions with an increase in the number of L-proline molecules/zwitterions in solutions, which in turn may cause more frictional resistance to the flow of solutions. The viscosity values of all of the systems under investigation exhibit a decreasing trend of variation with an increase in temperature. An increase in temperature may increase the kinetic energy of molecules, which in turn may decrease the hydrophilic–ionic and hydrophilic–hydrophobic interactions. The viscosity data have been fitted to the Jones–Dole[35] equation of the form

$$\eta_r = \eta/\eta_o = 1 + Am^{1/2} + Bm \tag{8}$$

where η_r is the relative viscosity of the solution, m is the molal concentration of solution, and η and η_o are the viscosities of solution and solvent, respectively. A, the Falkenhagen coefficient, represents the solute–solute interactions associated with the size and shape of solute, and B is a measure of structural modifications induced by the solute–solvent interactions.[36,37] The plots of $(\eta/\eta_o - 1)/m^{1/2}$ versus $m^{1/2}$ have been found to be linear at all temperatures of study in accordance with the Jones–Dole equation. The A- and B-coefficient values are the intercept and slope of the straight line, respectively, obtained from linear regression. The B-coefficient values have been given in the Table S3 of Supporting Information. The A-coefficient which reflect solute–solute interactions, are usually small and negligible in case of nonelectrolytes;[38] therefore, it is often ignored in nonelectrolyte systems. The temperature derivative of B-coefficient ($\mathrm{d}B/\mathrm{d}T$) has been also calculated. The positive and negative signs of $\mathrm{d}B/\mathrm{d}T$ values provide important information regarding the structure-making or structure-breaking ability of the solute in solvent media.[39,40] The negative and positive values of $\mathrm{d}B/\mathrm{d}T$ are for structure-maker and structure-breaker solutes in solution, respectively. The positive $\mathrm{d}B/\mathrm{d}T$ value for L-proline in aqueous glucose and aqueous sucrose solvents indicates that L-proline acts as a structure-breaker in both solvents. Sandhu and Singh[41] have reported the similar structure-breaker tendency of L-proline and L-hydroxyproline in methanol.

CONCLUSIONS

The higher $\Delta_{tr}\phi_V^o$ values of L-proline in 1 mol·L^{-1} aqueous sucrose solution than those in 1 mol·L^{-1} aqueous glucose solution is due to the stronger hydrophilic–ionic interactions between OH groups of sucrose molecules and zwitterionic center of L-proline in 1 mol·L^{-1} aqueous sucrose solution. The decrease in $\Delta_{tr}\phi_V^o$ values with increase in temperature indicates the corresponding decrease in number of electrostricted water molecules in the solution. The positive $\Delta_{tr}\phi_K^o$ values suggest the release of water molecules from the secondary solvation layer of L-proline zwitterion into the bulk. The decrease in $\Delta_{tr}\phi_K^o$ values with increase in temperature indicates the release of a smaller amount of water molecules from the secondary solvation layer of L-proline zwitterions into the bulk. The L-proline acts as a structure-maker in both aqueous glucose and in aqueous sucrose solvents. The ionic–hydrophilic interactions have been found to dominate over hydrophobic–hydrophilic interactions.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Partial molar volumes and compressibilities of L-proline (Table S1), transfer partial molar volumes and compressibilities as a function of temperature (Table S2), and viscosity B-coefficients at different temperatures (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

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

Funding Sources

Financial support from the UGC-SAP (DRS-I) scheme is acknowledged.

ACKNOWLEDGMENT

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

REFERENCES

(1) Taravati, A.; Shokrzadeh, M.; Ebadi, A. G.; Valipour, P.; Hassan, A. T. M.; Farrokhi, F. Various effects of sugar and polyols on the protein structure and function: Role as osmolyte on protein stability. *World Appl. Sci. J.* **2007**, *2*, 353–362.

(2) Kim, Y. K.; Chang, B. S.; Carpenter, J. F.; Jones, L. S.; Manning, M. C.; Dong, A.; Kendrick, B. S.; Randolph, T. W.; Carpenter, J. F. Effects of sucrose on conformational equilibria and fluctuations within the native-state ensemble of proteins. *Protein Sci.* **2003**, *12*, 1252–1261.

(3) Ebel, C.; Eisenberg, H.; Ghirlando, R. Probing protein-sugar interactions. *Biophys. J.* **2000**, *78*, 385–393.

(4) Arakawa, T.; Timasheff, S. N. Stabilization of protein structure by sugars. *Biochemistry* **1982**, *21*, 6536–6544.

(5) Lou, Y.; Lin, R. Enthalpy of transfer of amino acids from water to aqueous glucose solutions at 298.15 K. *Thermochim. Acta* **1998**, *316*, 145–148.

(6) Nain, A. K.; Pal, R.; Sharma, R. K. Volumetric, ultrasonic, and viscometric behaviour of L-histidine in aqueous-glucose solutions at different temperatures. *J. Chem. Thermodyn.* **2011**, *43*, 603–612.

(7) Pal, A.; Chauhan, N. Interactions of diglycine in aqueous saccharide solutions at varying temperatures: A volumetric, ultrasonic and viscometric Study. *J. Solution Chem.* **2010**, *39*, 1636–1652.

(8) Pal, A.; Chauhan, N. Volumetric, viscometric, and acoustic behaviour of diglycine in aqueous saccharide solutions at different temperatures. *J. Mol. Liq.* **2009**, *149*, 29–36.

(9) Pal, A.; Chauhan, N. Densities, speeds of sound and viscosities of L-alanine in aqueous fructose, maltose and lactose solutions at different temperatures. *Indian J. Chem.* **2009**, *48A*, 1069–1077.

(10) Pal, A.; Kumar, S. Volumetric properties of L-alanine, and L-valine in aqueous sucrose solutions at T = (288.15 and 308.15) K. *J. Chem. Thermodyn.* **2005**, *37*, 1085–1092.

(11) Palani, R.; Geetha, A. Acoustical and thermodynamical studies of L-serine, L-glutamine, and L-asparagine in aqueous D-glucose solutions at 298.15 K. *Res. J. Phys.* **2007**, *1*, 82–89.

(12) Ali, A.; Hyder, S.; Sabir, S.; Chand, D.; Nain, A. K. Volumetric, viscometric, and refractive index behaviour of α-amino acids and their groups contribution in aqueous D-glucose solution at different temperatures. *J. Chem. Thermodyn.* **2006**, *38*, 136–143.

(13) Li, S.; Sang, B. W.; Lin, R. Partial molar volumes of glycine, L-alanine, and L-serine in aqueous glucose solutions at T = 298.15 K. *J. Chem. Thermodyn.* **2002**, *34*, 1761–1768.

(14) Zhao, C.; Ma, P.; Li, J. Partial molar volumes and viscosity B-coefficients of arginine in aqueous glucose, sucrose and L-ascorbic acid solutions at T = 298.15 K. *J. Chem. Thermodyn.* **2005**, *37*, 37–42.

(15) Banipal, T. S.; Sehgal, G. Partial molal adiabatic compressibilities of transfer of some amino acids and peptides from water to aqueous sodium chloride and aqueous glucose solutions. *Thermochim. Acta* **1995**, *262*, 175–183.

(16) Kestin, J.; Sokolov, M.; Wakeham, W. A. Viscosity of liquid water in range 8 to 150 °C. *J. Phys. Chem. Ref. Data* **1978**, *7*, 941–948.

(17) Hedwig, G. R.; Reading, J. F.; Lilley, T. H. Aqueous solutions containing amino acids and peptides. Part 2. Partial molar heat capacities and partial molar volumes of some *N*-acetyl amino acid amides, some *N*-acetyl peptide amides and two peptides at 25 °C. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1751–1758.

(18) Desnoyers, J. E. Structural effects in aqueous solutions: a thermodynamic approach. *Pure Appl. Chem.* **1982**, *54*, 1469–1478.

(19) Gurney, R. W. *Ionic processes in solution*; McGraw Hill: New York, 1953.

(20) Frank, H. S.; Evans, M. W. Free volume and entropy in condensed systems III. Entropy in binary liquid mixtures; Partial molal entropy in dilute solutions; Structure and thermodynamics in aqueous electrolytes. *J. Chem. Phys.* **1945**, *13*, 507–532.

(21) Bhat, R.; Kishore, N.; Ahluwalia, J. C. Thermodynamic studies of transfer of some amino acids and peptides from water to aqueous glucose and sucrose solutions at 298.15 K. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2651–2665.

(22) Mishra, A. K.; Ahluwalia, J. C. Apparent molal volumes of amino acids, N-acetylamino acids, and peptides in aqueous solution. *J. Phys. Chem.* **1984**, *88*, 86–92.

(23) Hedwig, G. R.; Hoiland, H. Thermodynamic properties of peptide solutions 9. Partial molar isentropic pressure coefficients in aqueous solutions of sequence isomeric tripeptides with a single -CH_3 side-chain. *J. Chem. Thermodyn.* **1993**, *25*, 349–354.

(24) Riyazuddeen; Usmani, M. A. Interactions in (glycylglycine + 1 M aqueous glucose/1 M aqueous sucrose) systems at (298.15 to 323.15) K. *Thermochim. Acta* **2011**, DOI: 10.1016/j.tca.2011.03.024.

(25) Ali, A.; Khan, S.; Nabi, F. Volumetric, viscometric and refractive index behaviour of amino acids in aqueous glycerol at different temperatures. *J. Serb. Chem. Soc.* **2007**, *72*, 495–512.

(26) Wadi, R. K.; Ramasami, P. Partial molal volumes and adiabatic compressibilities of transfer of glycine and DL-alanine from water to aqueous sodium sulfate at 288.15, 298.15 and 308.15 K. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 243–247.

(27) Liu, H.; Lin, R.; Zhang, H. Enthalpic interactions of amino acids with saccharides in aqueous solutions at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 416–420.

(28) Pal, A.; Chauhan, N. Partial molar volumes, expansibilities and compressibilities of glyglyglycine in aqueous sucrose and fructose solutions between 288.15 and 308.15 K. *Thermochim. Acta* **2011**, *513*, 68–74.

(29) Rodriguez, H.; Soto, A.; Arce, A.; Khoshkbarchi, M. K. Apparent molar volume, isentropic compressibility, refractive index, and viscosity of DL-alanine in aqueous NaCl solutions. *J. Solution Chem.* **2003**, *32*, 53–63.

(30) Soto, A.; Arce, A.; Khoshkbarchi, M. K. Thermodynamics of Diglycine and Triglycine in Aqueous NaCl Solutions: Apparent Molar Volume, Isentropic Compressibility, and Refractive Index. *J. Solution Chem.* **2004**, *33*, 11–21.

(31) 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.

(32) Bernal, P. J.; Hook, W. A. V. Apparent molar volumes, isobaric expansion coefficients, and isentropic compressibilities, and their H/D isotope effects for some aqueous carbohydrate solutions. *J. Chem. Thermodyn.* **1986**, *18*, 955–968.

(33) Banipal, P. K.; Banipal, T. S.; Lark, B. S.; Ahluwalia, J. C. Partial molar heat capacities and volumes of some mono-, di- and tri-saccharides in water at 298.15, 308.15 and 318.15 K. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 81–87.

(34) Banipal, P. K.; Gautam, S.; Dua, S.; Banipal, T. S. Effect of ammonium salts on the volumetric and viscometric behavior of D(+)-glucose, D(−)-fructose and sucrose in aqueous solutions at 25 °C. *J. Solution Chem.* **2006**, *35*, 815–844.

(35) Jones, G.; Dole, M. The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J. Am. Chem. Soc.* **1929**, *51*, 2950–2964.

(36) Bai, T. C.; Yan, G. B. Viscosity *B*-coefficients and activation parametres for viscous flow of a solution of heptane dioic acid in aqueous sucrose solution. *Carbohydr. Res.* **1999**, *338*, 2921–2927.

(37) Kay, R. L.; Vituccio, T.; Zawoyski, C.; Evans, D. F. Viscosity *B*-coefficients for the tetraalkylammonium halides. *J. Phys. Chem.* **1966**, *70*, 2336–2341.

(38) Jenkins, H. D. B.; Marcus, Y. Viscosity *B*-coefficients of ions in solution. *Chem. Rev.* **1995**, *95*, 2695–2724.

(39) Feakins, D.; Freemantle, D. J.; Lawrence, K. G. Transition state treatment of the relative viscosity of electrolytic solutions. Applications to aqueous, non-aqueous and methanol + water systems. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 795–806.

(40) Kaminsky, M. Ion-solvent interaction and the viscosity of strong-electrolyte solutions. *Discuss. Faraday Soc.* **1957**, *24*, 171–179.

(41) Sandhu, J. S.; Singh, G. Viscosity *B*-coefficients of L-proline and L-hydroxyproline and the effect of added methanol. *J. Indian Chem. Soc.* **1988**, *65*, 173–176.