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Volumetric and Acoustic Properties of D(+) Glucosamine·HCl and L-Lysine·HCl in Aqueous Solutions at Different Temperatures

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In present work, density and speed of sound of aqueous binary mixtures of biologically important amino acid derivatives namely D(+) glucosamine·HCl and L-lysine·HCl have been measured at three different temperatures *i.e.* (278.15, 288.15 and 298.15) K and in the concentration range of 0.0-0.2 mol kg^{-1}. Using density and speed of sound data, different thermodynamic and acoustic parameters like apparent molar volume (V_ϕ) and apparent molar isentropic compression (K_ϕ) of solute have been computed at different temperatures. Speed of sound data have also been used to calculate hydration number (n_H) of solute. The temperature dependence of the limiting apparent molar volume of solute has been used to calculate thermal expansion coefficient (α^*), apparent molar expansivity (E^0_ϕ) of solute and Hepler's constant ($\partial^2 V^0_\phi/\partial T^2$). The final outcome of the study has been discussed in terms of various interactions among solute and solvent molecules.

Keywords: Density, Apparent molar volume, Isentropic compressibility, Hydration number, D(+) Glucosamine·HCl, L-lysine·HCl.

INTRODUCTION

The interactions of different functional groups in proteins with the surrounding environment play an important role in their conformational characteristics. The salt solutions are known to produce large effects on the properties and structure of proteins such as their solubility, stability, denaturation, and dissociation into subunits, *etc.* [1]. Due to complex structure of proteins, the study of conformational stability and unfolding behaviour of globular proteins has proved quite challenging and still remains a subject of extensive investigations [2]. The thermodynamic properties of a completely unfolded protein system can be estimated by adding together the contributions of the small structural units that constitute its molecular sequence. Therefore, protein model compounds such as amino acids and peptides have been investigated with respect to different thermodynamic properties in water and in mixed aqueous solutions [3-12]. Salt solutions influence the stability and structure of proteins. To understand the physico-chemical behaviour of different mixtures and the nature of interaction of molecules in binary mixtures, it is important to analyze the thermodynamic and acoustic properties. Remarkable experimental work has been reported on the thermodynamic properties of amino acids [3-12], vitamins [13-15] and proteins [16,17] in aqueous solution, but few studies exist on the volumetric and acoustic properties of amino acid derivatives in aqueous solutions [18].

The systematic study of amino acid derivatives can provide valuable information about their behaviour in solutions and insight into the conformational stability of proteins. Hence, in continuation of previous studies [19,20], we have undertaken a systematic study on volumetric and acoustic properties of binary mixtures of two amino acid derivatives *i.e.* D(+) glucosamine HCl + water and L-lysine HCl + water. In the present work, we report herewith the experimental data of density and speed of sound of aqueous binary mixtures of amino acid derivatives, D(+) glucosamine HCl and L-lysine HCl at three different temperatures *i.e.* (278.15, 288.15 and 298.15) K within the concentration range of 0.0-0.2 mol kg^{-1}. Using the experimental results, different derived parameters, *viz.*, apparent molar volume (V_ϕ) of solute, isentropic compressibility (κ_s) of solution, apparent molar isentropic compression (K_ϕ) of solute, limiting apparent molar volume (V_ϕ^0) of solute, limiting apparent molar isentropic compression (K_ϕ^0) of solute, coefficient of thermal expansion (α^*), limiting apparent molar expansivity (E_ϕ^0) of solute, ($\partial^2V_\phi^0/\partial T^2$) and hydration number ($n_H$) have been computed.

EXPERIMENTAL

In present study, chemicals *viz.* D(+) glucosamine·HCl and L-Lysine·HCl had been procured from Sigma-Aldrich, USA. The specifications of these compounds are given in Table-1. These solutes were used without further purification, however, before use, were dried in a vacuum oven at 343.15 K till the last two weights were constant. These were kept over anhydrous-fused calcium chloride in vacuum desiccators for more than two days. All the binary mixtures were prepared in freshly prepared doubly distilled water on a molality basis by using Mettler (Switzerland) balance with a precision of ± 0.1 mg. The relative uncertainties $u_r(m)$ in the molality of the solutions are within ± 1%.

The densities (ρ) of both studied aqueous binary systems at 278.15 K were measured by using Lypkin's modified bicapillary pycknometers. The density of pure water was taken from the literature [21]. The pycnometers were calibrated by measuring the densities of aqueous solutions of sodium chloride in the low concentration range at 278.15 K. The density values agreed well with the literature values [22] up to ± 0.05 kg m^{-3}. The combined expanded uncertainty was $U_\rho(\rho) = 0.1$ kg m^{-3}. The details are given elsewhere [23].

The speed of sound measurements of studied binary systems at 278.15 K were carried out by using variable path ultrasonic interferometer (Model S1-2M/S Dr. Steeg and Reuter, Germany) at a resonating frequency of 2 MHz (single crystal). The interferometer was calibrated by measuring the speeds of sound in freshly prepared doubly distilled water at 278.15 K. The values of speed of sound in the present work were reproducible [24] within ± 0.5 m s^{-1}. The details of sound velocity measurements are given elsewhere [25].

The densities (ρ) and speeds of sound (u) of studied aqueous binary systems were measured by using Anton Paar DSA 5000 M densimeter at 288.15 and 298.15 K which was calibrated with freshly prepared doubly distilled water and air. The syringe was used to insert the sample in the instrument. The temperature of the densimeter was controlled *via* built-in Peltier thermostat instrument having temperature constancy of ± 0.01 K. The uncertainties in the measurements of density [22] and sound velocity [25] were ± 0.05 kg m^{-3} and ± 0.5 m s^{-1}, respectively. The combined expanded uncertainties in the measurements of density and speed of sound were $U_\rho(\rho) = 0.1$ kg m^{-3} and $U_u(u) = 1.0$ m s^{-1}, respectively.

RESULTS AND DISCUSSION

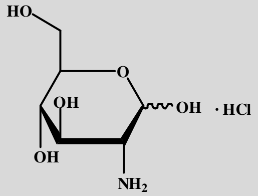
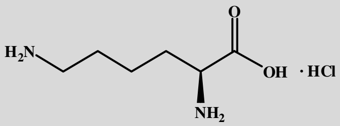
The experimentally measured values of density and speed of sound of aqueous binary solutions of D(+) glucosamine ·HCl and L-Lysine·HCl at 278.15, 288.15 and 298.15 K are given in Tables 2 and 3, respectively. A representative 3D-plot of density with temperature and molality of aqueous solutions of D(+) glucosamine HCl and L-lysine HCl has been shown in Fig. 1. It can be seen that density of the solution increases linearly with increase in concentration of solute in the solution. Fig. 1 shows that the density of solution decreases slightly with increase in the temperature of solution at a particular concentration for both the studied aqueous binary systems.

Volumetric properties: The apparent molar volumes (V_ϕ) of D(+) glucosamine·HCl and L-lysine·HCl in aqueous binary solutions at different temperatures have been calculated from the experimental values of densities using the following equation. The values of V_ϕ at different temperatures are listed in Tables 2 and 3, respectively.

$$V_\phi = \frac{M}{\rho} - \frac{(\rho - \rho_0)}{m\rho\rho_0} \qquad (1)$$

where, M denotes the molar mass (kg mol^{-1}), m denotes the molality (mol kg^{-1}) of the solution, and ρ_0 and ρ denote densities of solvent and solution, respectively. The probable uncertainty in the V_ϕ values at lowest concentration (m = 0.05 mol kg^{-1}) is found to be ± 1 × 10^{-6} m^3 mol^{-1} at studied temperatures. Whereas, the uncertainty in the V_ϕ values at the highest concentration

TABLE-1
PROVENANCE AND MASS FRACTION PURITY OF THE CHEMICALS USED

Chemical name	Provenance	CAS No.	Mass fraction purity[a]	Analysis method[b]	Molar mass (g mol^{-1})	Structure
D(+) Glucosamine·HCl	Sigma Aldrich, U.S.A.	66-84-2	≥ 0.99	TLC[b]	215.63	
L-Lysine·HCl	Sigma Aldrich, U.S.A.	657-27-2	≥ 0.98	HPLC[c]	182.65	

[a]As provided by supplier. [b]Thin layer chromatography. [c]High performance liquid chromatography.

TABLE-2
DENSITY (ρ), SPEED OF SOUND (u), APPARENT MOLAR VOLUME OF SOLUTE (V_ϕ), ISENTROPIC COMPRESSIBILITY (κ_s) OF SOLUTION, APPARENT MOLAR ISENTROPIC COMPRESSION (K_ϕ) OF SOLUTE FOR AQUEOUS BINARY MIXTURES OF D(+) GLUCOSAMINE·HCl AT 278.15, 288.15 AND 298.15 K AND AT PRESSURE 1.013×10^5 N m^{-2}

m (mol kg^{-1})	$10^{-3}\cdot\rho$ (kg m^{-3})	u (m s^{-1})	$10^6\cdot V_\phi$ (m^3 mol^{-1})	$10^{11}\cdot\kappa_s$ (m^2 N^{-1})	$10^{15}\cdot K_\phi$ (m^5 N^{-1} mol^{-1})
278.15 K					
0.0000	0.99996	1426.2	124.40	49.17	-57.94
0.0403	1.00358	1430.2	125.43	48.71	-51.47
0.0501	1.00444	1431.1	125.67	48.61	-50.05
0.0603	1.00529	1432.2	126.63	48.50	-50.06
0.0701	1.00608	1433.2	127.56	48.39	-49.30
0.0802	1.00694	1434.2	127.73	48.28	-48.91
0.0901	1.00778	1435.1	127.93	48.18	-47.88
0.1002	1.00863	1436.1	128.04	48.07	-47.72
0.1101	1.00947	1436.9	128.09	47.98	-46.46
0.1202	1.01033	1437.9	128.07	47.87	-46.50
0.1302	1.01109	1438.9	128.75	47.77	-45.90
0.1402	1.01191	1439.9	128.88	47.66	-45.81
288.15 K					
0.0000	0.99910	1465.9	126.80	46.58	-51.92
0.0502	1.00350	1471.0	127.54	46.05	-45.56
0.0601	1.00430	1472.2	128.43	45.94	-46.82
0.0701	1.00510	1473.3	129.26	45.84	-46.49
0.0802	1.00596	1474.4	129.34	45.73	-46.55
0.0899	1.00678	1475.2	129.26	45.64	-45.03
0.0997	1.00760	1476.3	129.32	45.54	-45.46
0.1100	1.00842	1477.2	129.71	45.44	-44.07
0.1197	1.00924	1478.3	129.65	45.34	-44.61
0.1296	1.00999	1479.3	130.23	45.24	-43.88
0.1403	1.01085	1480.5	130.37	45.13	-44.13
0.1500	1.01163	1481.2	130.47	45.06	-42.68
0.1601	1.01247	1482.2	130.43	44.96	-42.53
298.15 K					
0.0000	0.99705	1496.7	130.60	44.77	-43.91
0.0495	1.00121	1501.5	131.16	44.30	-37.82
0.0590	1.00198	1502.4	131.47	44.21	-37.05
0.0699	1.00288	1503.6	131.65	44.10	-38.10
0.0789	1.00364	1504.2	131.41	44.04	-35.82
0.0901	1.00460	1505.0	130.97	43.95	-34.38
0.1002	1.00540	1506.2	131.36	43.84	-35.64
0.1102	1.00622	1506.8	131.28	43.77	-33.61
0.1202	1.00701	1507.6	131.54	43.69	-33.01
0.1301	1.00776	1509.1	132.06	43.57	-34.94
0.1401	1.00860	1509.5	131.75	43.51	-32.81
0.1500	1.00942	1510.9	131.65	43.40	-34.78
0.1597	1.01016	1511.3	131.91	43.34	-32.60

[a] Standard uncertainties σ are σ(T) = 0.002 K at 278.15 K and 0.01 K at 288.15 K and 298.15 K: $u_r(m)$ = 1%: σ(p) = 1% and the combined expanded uncertainty $U_\rho(\rho)$ = 0.1 kg m^{-3} (k = 2) with 0.95 level of confidence.

[b] Standard uncertainties σ are σ(T) = 0.1 K at 278.15 K and 0.01 K at 288.15 K and 298.15 K: $u_r(m)$ = 1% and the combined expanded uncertainty U_u (u) = 1.0 m s^{-1} (k = 2) with 0.95 level of confidence.

TABLE-3
DENSITY (ρ)[a], SPEED OF SOUND (u)[b], APPARENT MOLAR VOLUME (V_ϕ) OF SOLUTE, ISENTROPIC COMPRESSIBILITY (κ_s) OF SOLUTION, APPARENT MOLAR ISENTROPIC COMPRESSION (K_ϕ) OF SOLUTE OF AQUEOUS SOLUTIONS OF L-LYSINE·HCl AT 278.15, 288.15 AND 298.15) AND AT PRESSURE 1.013×10^5 N m^{-2}

m (mol kg^{-1})	$10^{-3}\cdot\rho$ (kg m^{-3})	u (m s^{-1})	$10^6\cdot V_\phi$ (m^3 mol^{-1})	$10^{11}\cdot\kappa_s$ (m^2 N^{-1})	$10^{15}\cdot K_\phi$ (m^5 N^{-1} mol^{-1})
278.15 K					
0.0000	0.99996	1426.2	121.10	49.17	-78.28
0.0506	1.00303	1434.0	121.59	48.48	-76.51
0.0653	1.00387	1436.3	122.32	48.29	-75.84
0.0801	1.00476	1438.7	122.17	48.08	-76.57
0.0904	1.00535	1440.3	122.39	47.95	-76.18
0.1001	1.00589	1441.8	122.67	47.82	-75.68
0.1101	1.00654	1443.3	122.12	47.69	-75.67
0.1197	1.00703	1444.8	122.74	47.57	-74.97
0.1348	1.00792	1447.2	122.63	47.37	-75.19
0.1504	1.00884	1449.6	122.52	47.17	-74.93
0.1653	1.00972	1451.9	122.41	46.98	-74.77
0.1793	1.01046	1454.1	122.80	46.80	-74.30
0.2092	1.01222	1458.8	122.59	46.42	-74.26
288.15 K					
0.0000	0.99910	1465.9	122.10	46.58	-71.29
0.0505	1.00240	1473.5	123.07	45.95	-70.91
0.0658	1.00299	1475.6	123.47	45.79	-63.30
0.0802	1.00381	1477.8	123.47	45.62	-63.44
0.0903	1.00441	1478.8	123.29	45.53	-60.10
0.1005	1.00500	1481.1	123.24	45.36	-65.34
0.1101	1.00556	1482.2	123.23	45.27	-63.29
0.1198	1.00610	1483.3	123.37	45.18	-61.36
0.1352	1.00692	1485.9	123.88	44.98	-62.43
0.1499	1.00765	1488.0	124.61	44.82	-61.31
0.1652	1.00860	1490.3	124.01	44.64	-61.90
0.1801	1.00948	1492.6	123.82	44.46	-62.27
0.2000	1.01055	1495.7	124.03	44.23	-62.39
298.15 K					
0.0000	0.99705	1496.7	124.80	44.77	-60.65
0.0503	0.99991	1503.9	125.52	44.22	-54.69
0.0651	1.00074	1505.8	125.70	44.07	-52.84
0.0801	1.00160	1508.0	125.43	43.90	-54.11
0.0896	1.00213	1509.2	125.46	43.81	-52.49
0.1003	1.00269	1510.5	125.89	43.71	-51.01
0.1105	1.00328	1511.9	125.64	43.61	-51.16
0.1204	1.00383	1513.2	125.63	43.51	-50.80
0.1348	1.00442	1515.0	127.22	43.38	-48.81
0.1504	1.00547	1517.1	125.83	43.21	-49.75
0.1651	1.00626	1519.2	125.92	43.06	-50.00
0.1806	1.00701	1521.4	126.43	42.90	-49.66
0.1997	1.00808	1523.4	126.23	42.75	-47.83

[a] Standard uncertainties σ are σ(T) = 0.002 K at 278.15 K and 0.01 K at 288.15 K and 298.15 K: $u_r(m)$ = 1%: σ(p) = 1% and the combined expanded uncertainty $U_\rho(\rho)$ = 0.1 kg m^{-3} (k = 2) with 0.95 level of confidence.

[b] Standard uncertainties σ are σ(T) = 0.1 K at 278.15 K and 0.01 K at 288.15 K and 298.15 K: $u_r(m)$ = 1% and the combined expanded uncertainty U_u (u) = 1.0 m s^{-1} (k = 2) with 0.95 level of confidence.

(m = 0.2 mol kg^{-1}) was estimated to be equal to ± 0.25 × 10^{-6} m^3 mol^{-1}.

It is observed that the value of apparent molar volume (V_ϕ) at a particular concentration increases with increase in temperatureof the solution (Tables 2 and 3), indicating the presence of strong solute-solvent interactions in the studied aqueous binary systems, and these interactions are further strengthened with rise in temperatures.

The limiting apparent molal volume of the solute in dilute aqueous solution is obtained by using the following equation:

$$V_\phi = V_\phi^0 + A_v(m)^{1/2} + S_v m \qquad (2)$$

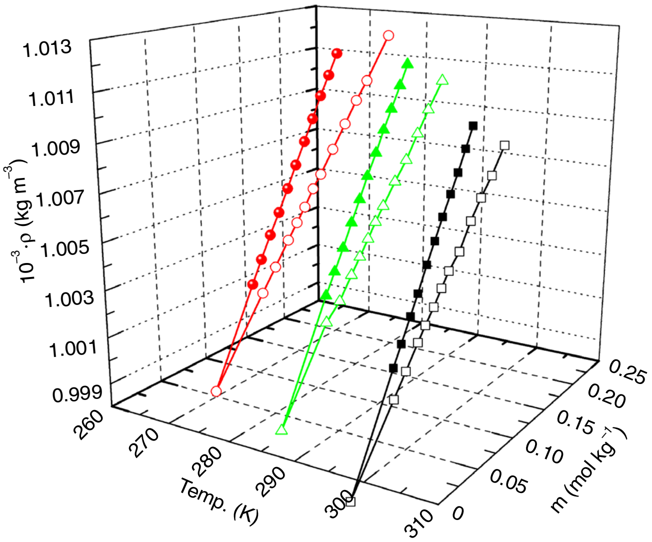


Fig. 1. 3D-plot of density with temperature and molality of aqueous solutions of D(+) glucosamine·HCl at T = 278.15 K: ●–●, 288.15 K: ▲–▲, 298.15 K: ■–■, and L-lysine·HCl at 278.15 K: ○–○, 288.15 K: △–△, 298.15 K: □–□

where, V_ϕ is apparent molar volume of solute, m is the molality of the solution, V_ϕ^0 is limiting apparent molar volume, S_v is the volumetric pairwise interaction coefficient [26] and A_v is the Debye-Hückel limiting slope for dilute electrolytic solutions [27]. The limiting value of the apparent molar volume of the solute, describes the change of the volume when 1 mol of the solute is added to the infinite amount of solvent. This value equals the standard partial molar volume of the solute and is useful quantity to study the solute-solvent interactions in solutions [28]. In order to evaluate V_ϕ^0 at different temperatures, eqn. 2 was rearranged and $(V_\phi - A_v\,(m)^{1/2})$ is plotted against m, the intercept of the curve gives V_ϕ^0 and slope gives S_v (Fig. 2).

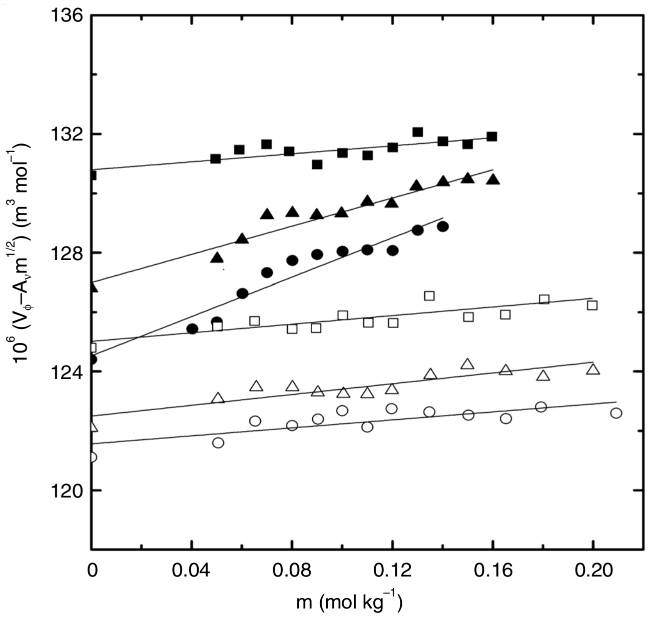


Fig. 2. Plot of (V_ϕ–$A_V\sqrt{m}$) against molality (m) of aqueous solutions of D(+) glucosamine·HCl at T = 278.15 K: ●–●, 288.15 K: ▲–▲, 298.15 K: ■–■, and L-lysine·HCl at 278.15 K: ○–○, 288.15 K: △–△, 298.15 K: □–□

The V_ϕ^0 values reflect the true volume of the solute and the volume change arising from solute + solvent interactions. The estimated uncertainties in V_ϕ^0 values are represented by the standard deviation (σ) and average absolute deviation (AAD), which is equal to the root mean square of the deviation between the experimental and calculated V_ϕ for each data point. These were evaluated using the following expressions, respectively.

$$\sigma = \left\{\sum\left(F(x)_{exp} - F(x)_{calcd}\right)/(n-1)\right\}^{1/2} \qquad (3)$$

$$AAD = \left\{\sum\left(F(x)_{exp} - F(x)_{calcd}\right)/(n-1)\right\} \qquad (4)$$

The V_ϕ^0, S_v, σ and AAD values of the studied aqueous binary systems are listed in Table-4. The obtained values of V_ϕ^0 for aqueous binary mixtures of L-lysine HCl *i.e.* (121.1, 122.2 and 124.8) × 10^{-6} m^3 mol^{-1}, at 278.15, 288.15 and 298.15 K, respectively were found to be in excellent agreement with those reported by Yasuda *et al.* [18] as (121.5, 123.2 and 124.8) × 10^{-6} m^3 mol^{-1}, respectively. It is found that all the values of V_ϕ^0 are positive, suggesting the existence of the strong solute-solvent interactions. It is seen from Table-4 that V_ϕ^0 value increases with rise in temperature of the solution signifying that when the amino acid derivative is transferred to the infinitely dilute solution in water, there could be structuring of the solvent molecules near the non-polar groups (hydrophobic hydration). This effect decreases with increase in temperature but the hydrophilic hydration increases with a larger number of solvent molecules hydrating the zwitterions, leading to the increase of V_ϕ^0 values with increase in temperature [29,30].

According to co-sphere overlap model [31], the overlap of the co-sphere of an ion with that of hydrophobic groups results in a negative volume change. On the other hand, the overlap of the co-spheres of two ions with that of a hydrophilic group produces a positive volume change. The increase in V_ϕ^0 values of both the solutes with an increase in temperature from 278.15 K to 298.15 K, in aqueous solution can be explained by considering the size of primary and secondary solvation layers around the zwitterions of D(+) glucosamine HCl or L-lysine HCl. The water molecules from the secondary solvation layer of D(+) glucosamine HCl or L-lysine HCl zwitterions are released into the bulk of the water, which results in the larger V_ϕ^0 values of D(+) glucosamine HCl or L-lysine HCl at higher temperatures [32]. Table-4 shows that the value of V_ϕ^0 for D(+) glucosamine HCl at a particular tempe-rature is greater than that of L-lysine HCl.

The value of S_v obtained from eqn. 2 is the volumetric virial coefficient and it characterizes the pairwise interaction of solvated species in solution [33]. It is evident that the values S_v for (D(+) glucosamine·HCl + water) and (L-lysine·HCl + water) binary systems are positive at all the studied temperatures (Table-4). It is also observed that the values of S_v decrease with increase in temperature of the solution except for (lysine·HCl + water) at 278.15 K, suggesting the existence of strong ion-ion interactions in these binary systems [13]. It is also observed that the values of S_v are higher in the case of (D (+) glucosamine·HCl + water) than the (lysine·HCl + water)

TABLE-4
LIMITING APPARENT MOLAR VOLUME (V^0_ϕ) OF SOLUTE, STANDARD DEVIATION (σ) IN V^0_ϕ VALUES, ABSOLUTE AVERAGE DEVIATION (AAD) IN V^0_ϕ VALUES, EXPERIMENTAL SLOPE (S_V), LIMITING APPARENT MOLAR EXPANSIVITY (E^0_ϕ) OF SOLUTE AT 283.15 AND 293.15 K, COEFFICIENT OF THERMAL EXPANSION (α^*) AND $\partial^2V^0_\phi/\partial T^2$ AT 288.15 K FOR AQUEOUS BINARY SYSTEMS OF D (+) GLUCOSAMINE·HCl And L-LYSINE·HCl

Temp. (K)	$10^6 \cdot V^0_\phi$ ($m^3\ mol^{-1}$)	$10^6 \cdot \sigma$ ($m^3\ mol^{-1}$)	$10^6 \cdot$AAD ($m^3\ mol^{-1}$)	S_V	$10^6 \cdot E^0_\phi$ ($m^3\ mol^{-1}\ K^{-1}$)	$10^3 \cdot \alpha^*$ (K^{-1})	$\partial^2V^0_\phi/\partial T^2$ ($m^3\ mol^{-1}\ K^{-2}$)
D (+) Glucosamine·HCl + water							
278.15							
283.15	124.4	0.13	0.03	29.39	0.24		
288.15	126.8	0.10	0.02	19.71	0.38	2.44	0.014
293.15	130.6	0.07	0.02	2.319			
298.15							
L-Lysine·HCl + water							
278.15							
283.15	121.1	0.10	0.02	5.99	0.11		
288.15	122.2	0.10	0.02	6.54	0.26	1.51	0.015
293.15	124.8	0.12	0.03	3.61			
298.15							

binary system. A similar type of interactions has been also reported by Roy *et al.* [34].

To study the solute-solvent interaction occurring in liquid mixtures, $E^0_\phi = \frac{\partial V^0_\phi}{\partial T}$ *i.e.* the limiting apparent molar expansibility at infinite dilution could be considered as good measure to be reckoned. The calculated values of E^0_ϕ at 283.15 and 293.15 K for the two systems investigated are given in Table-4.

Table-4 shows that positive values of E^0_ϕ are obtained for both the studied aqueous binary systems which increase with increase in temperature. This might be due to the presence of caging effect [35]. It means that the solute molecules occupy the interstitial spaces in the aqueous system resulting in hydrophobic character. Some water molecules may be released from the hydration layers into the bulk of the solution, with increase in temperature. This would increase the solution volume a little more rapidly than that of the pure water. It is noted that the values of E^0_ϕ for studied aqueous binary systems appear to be consistent with those of other amino acid systems [36,37].

The behaviour of the second order derivatives of partial volume of solute at infinite dilution with respect to temperature could be understood by the relation $dE^0_\phi/dT = \partial V^0_\phi/\partial T^2$ and presented in Table-4. Hepler suggested that the sign of ($\partial^2 V^0_\phi/\partial T^2$) could be used to estimate the ability of solute to break or make the structure in the solvent [38]. Table-4 also shows that the values of $\partial^2 V^0_\phi/\partial T^2$ are positive for D(+) glucosamine·HCl as well as L-lysine·HCl suggesting the structure making (promoting) tendency of solutes when dissolved in water. Also, positive value of $\partial^2 V^0_\phi/\partial T^2$ indicates the predominance of hydrophobic hydration phenomenon over the electrostriction of water molecules around the solute molecules.

Coefficient of thermal expansion (α^*) can be used to understand interactions among solute-solvent molecules [39]. The values of thermal expansion coefficient (α^*) of studied solutes were calculated at 288.15 K using eqn. 5.

$$\alpha^* = \left(\frac{1}{V^0_\phi}\right)\left(\frac{\partial V^0_\phi}{\partial T}\right) \tag{5}$$

The values of α^* for both the systems are listed in Table-4. Thus, it is inferred that the value of α^* for aqueous solution of D(+) glucosamine·HCl is higher than that of the L-lysine·HCl. Hence, it can be concluded that interactions among solute and solvent molecules are stronger in aqueous mixture of (D(+) glucosamine·HCl + H_2O) than (L-lysine·HCl + H_2O).

Acoustic properties: A representative 3D-plot of speed of sound (u) in aqueous solution with temperature (278.15, 288.15 and 298.15) K and the molality of aqueous solutions of D(+) glucosamine·HCl and L-lysine·HCl has been depicted in Fig. 3. It is observed that the speed of sound increases with temperature at particular concentration and it increases with concentration at a particular temperature for both the systems, (D(+) glucosamine·HCl+ H_2O) and (L-lysine·HCl + H_2O). Density and speed of sound data were used to compute the isentropic compressibility (κ_s) of solution using following equation:

$$\kappa_s = \frac{1}{V} \cdot \left(\frac{\partial V}{\partial P}\right)_s = \left(\frac{1}{\rho . u^2}\right) \tag{6}$$

where, u is the speed of sound and ρ is the density of solution.

Fig. 4 shows the variation of isentropic compressibility (κ_s) of solution as a function of molality (m) of solution for the studied aqueous binary systems at three different temperatures (278.15, 288.15 and 298.15) K. Isentropic compressibility (κ_s) of solution decreases linearly with increase in concentration of solute in solution at a particular temperature and also decreases with the increase in the temperature at particular concentration of solute in the solution. The values of isentropic compressibility (κ_s) of aqueous solution of D(+) glucosamine·HCl and L-lysine·HCl are listed in Tables 2 and 3, respectively.

The apparent molar compression (K_ϕ) of solute in aqueous solutions at different temperatures was calculated using eqn. 7:

$$K_\phi = \left[\frac{(\rho_0 \kappa_s - \rho \kappa_{s0})}{m \rho \rho_0}\right] + \left[\frac{M \kappa_s}{\rho}\right] \tag{7}$$

where, m is the molality of the solution, M is the molar mass of the solute, ρ and ρ_0 are the densities of solution and solvent, respectively, and κ_s and κ_{s0} represent the values of isentropic compressibility of solution and pure solvent, respectively.

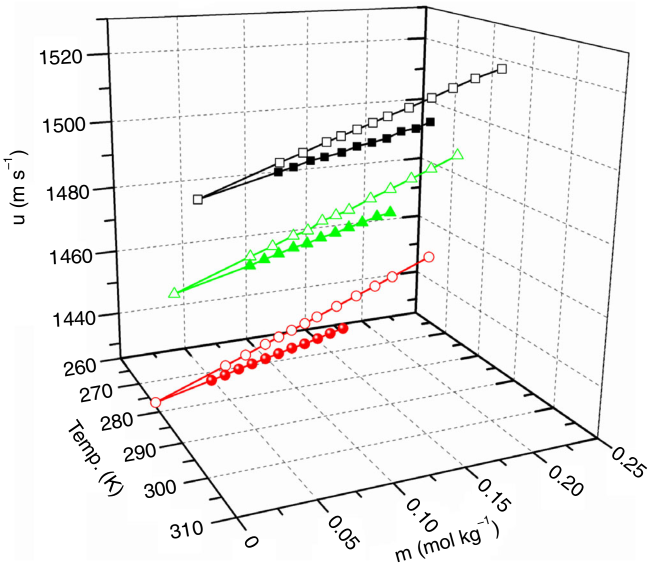


Fig. 3. 3D-plot of variation in speed of sound with temperature and molality of aqueous solutions of D(+) glucosamine·HCl at T = 278.15 K: ●–●, 288.15 K: ▲–▲, 298.15 K: ■–■, and L-lysine·HCl at 278.15 K: ○–○, 288.15 K: △–△, 298.15 K: □–□

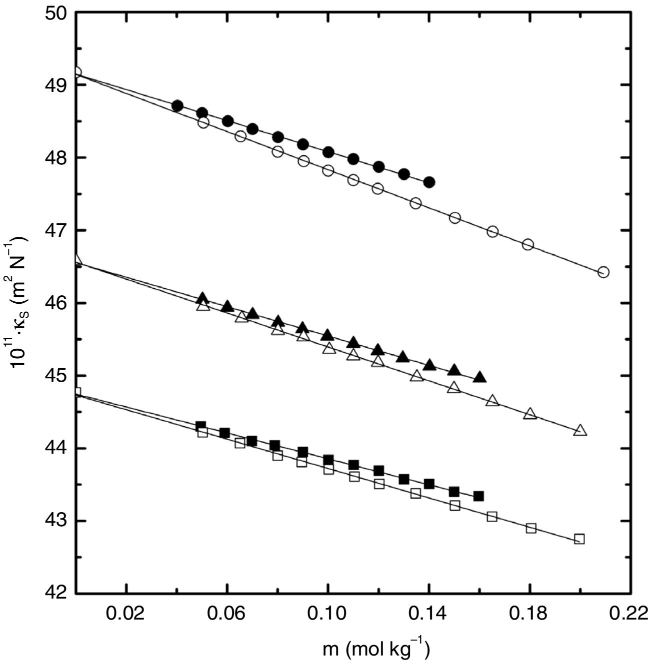


Fig. 4. Plot of variation in isentropic compressibility (κ_s) of the solution against molality (m) of aqueous solutions of D(+) glucosamine·HCl at T = 278.15 K: ●–●, 288.15 K: ▲–▲, 298.15 K: ■–■, and L-lysine·HCl at 278.15 K: ○–○, 288.15 K: △–△, 298.15 K: □–□

The calculated values of K_ϕ for D(+) glucosamine·HCl and L-lysine·HCl in aqueous solutions are listed in Tables 2 and 3, respectively. The uncertainty in the value of K_ϕ at lowest concentration by considering the uncertainty in isentropic compressibility (κ_s) as ± 0.05 × 10^{-11} m^2 N^{-1} was found to be ± 10 × 10^{-15} m^5 N^{-1} mol^{-1} and at highest concentration, it was found to be ± 2.5 ×10^{-15} m^5 N^{-1} mol^{-1}.

The limiting apparent molar isentropic compression (K_ϕ^0) of solute in aqueous medium for electrolytes have been calculated using following expression and are listed in Table-5.

$$K_\phi = K_\phi^0 + S_{KS}\cdot\sqrt{m} \qquad (8)$$

It is observed that K_ϕ^0 values are negative at all the temperatures studied in the present work. The negative K_ϕ^0 values show that water molecules around the ionic charge groups of solutes are less compressible than the water molecules present in the bulk solution because it is assumed that studied solutes are not pressure dependent and electrostricted water molecules are already compressed to their maximum extent by the charge on ions in the amino acid derivatives. Therefore, the compression of a solution is mainly due to the effect of pressure on the bulk water molecules. Hence, K_ϕ^0 is a measure of protection that the solute molecule gives to the solvent [40].

The variation in the values of apparent molar isentropic compression (K_ϕ) of solute is plotted against √m in Fig. 5 for aqueous binary systems of D(+) glucosamine·HCl and L-lysine ·HCl at studied temperatures. It is also observed that K_ϕ varies linearly with square root of molality of the solution and K_ϕ values become less negative with increase in temperature; this may be due to the fact that at lower temperature, water around the solute molecule is tightly bound to the solute and yields a high negative value of K_ϕ. Also, negative values of K_ϕ^0 indicate that the water molecules surrounding the amino acid derivatives would present greater resistance to compression than water molecules present in bulk. The more negative values of K_ϕ^0 for D(+) glucosamine·HCl and L-lysine·HCl at low temperature are attributed to the strong attractive interactions between amino acid derivatives and water [41].

Yasuda *et al.* [18] have reported the values of limiting apparent molal compression (K_ϕ^0) of L-lysine·HCl as (-78.6, -64.6 and -53.6) × 10^{-15} m^5 N^{-1} mol^{-1} at 278.15, 288.15 and 298.15 K, respectively. Present value at 278.15 K is in excellent agreement with their value while at 288.15 and 298.15 K, however, the current values are slightly higher than the reported ones. Due to unavailability of literature value for (D(+) glucosamine·HCl + water) binary system, the data was compared with the carbohydrate compounds like glucose. Due to the

TABLE-5
LIMITING APPARENT MOLAR ISENTROPIC COMPRESSION (K^0_ϕ) OF SOLUTE, EXPERIMENTAL SLOPE (S_K) AND COMPRESSIBILITY HYDRATION NUMBER (n_H) AT 278.15, 288.15 AND 298.15 K FOR BOTH STUDIED AQUEOUS BINARY ELECTROLYTIC SYSTEMS

Temp. (K)	D(+) Glucosamine·HCl + Water			L-Lysine·HCl + Water		
	$10^5\cdot K^0_\phi$ (m^5 N^{-1} mol^{-1})	S_K	n_H	$10^5\cdot K^0_\phi$ (m^5 N^{-1} mol^{-1})	S_K	n_H
278.15	-57.94	33.03	13.01	-78.28	08.49	15.54
288.15	-51.92	22.23	12.93	-71.29	23.69	14.43
298.15	-43.91	27.79	12.00	-60.65	28.02	12.66

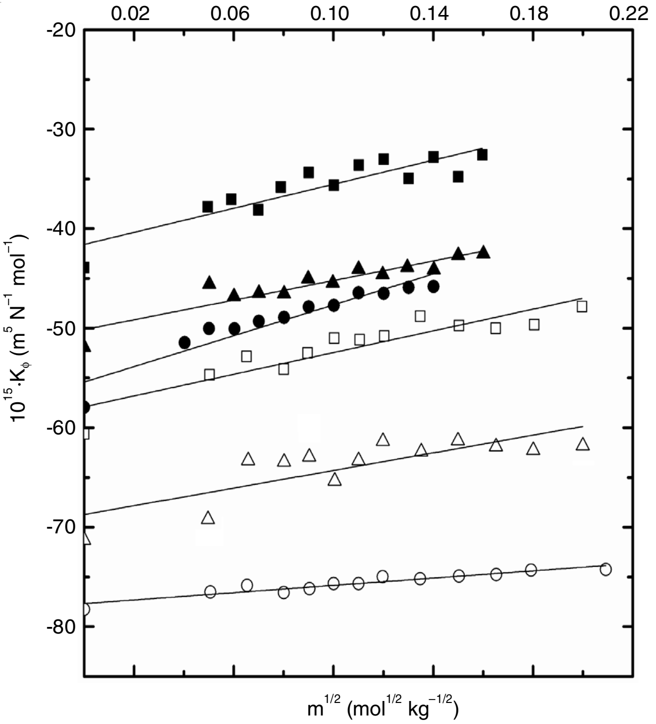


Fig. 5. Plot of K_ϕ of solute against $m^{1/2}$ of aqueous solutions of D(+) glucosamine·HCl at T = 278.15 K: ●–●, 288.15 K: ▲–▲, 298.15 K: ■–■, and L-lysine·HCl at 278.15 K: ○–○, 288.15 K: △–△, 298.15 K: □–□

presence of a large number of –OH groups, they are highly polar and can be hydrated easily. The polarity of the carbohydrate molecules depends on the orientation of the hydroxyl groups in the molecule. The V_ϕ^0 and K_ϕ^0 depend upon number of -OH and -NH_2 groups and their positions (equatorial or axial) in the molecule. The V_ϕ^0 for D(+) glucosamine·HCl is more than that of glucose [40]. Also, it is found that the K_ϕ^0 of D(+) glucosamine·HCl is more negative as compared to that of glucose [40,42].

Hydration behaviour: Hydration number refers to the average number of water molecules that are affected by interactions between the solute and solvent molecules and cause an observable effect on a physical property of the solution. Acoustic method is applied for the determination of hydration numbers using the values of isentropic compressibility. The link between compressibility and hydration is very insightful: compressibility decreases with pressure, because the decreasing intermolecular distances result in an increase in the intermolecular forces of repulsion, the limit of compressibility with pressure should be zero. On the other hand, hydration involves a strong force field in which the solute molecules are placed and thus acts the same as pressure.

The hydration number (n_H) of solute has been derived from the speed of sound data using Passynski equation (eqn. 9) [43]. The relative change of compressibility was assumed by Passynski as caused by engaging some fraction of water molecules in hydration spheres, where they become incompressible.

$$n_H = \frac{n_{H_2O}}{n_{solute}} \times \left(1 - \frac{\kappa_{s,solution}}{\kappa_{s,H_2O}}\right) \qquad (9)$$

where, n_{H_2O} and n_{solute} are the number of moles of water and solute in solution, respectively, $\kappa_{s,solution}$ is isentropic compressibility of the solution and κ_{s,H_2O} is isentropic compressibility of pure solvent.

After the addition of a solute into the water there are some molecules of water which become non-compressible, because they are now bonded to the guest molecule and excluded from the total compressibility, this phenomenon is called as hydration. Passynski [43] applied this idea to electrolytic solutions, supposing that water molecules undergo electrostrictive compression in electrostatic field of ions, which acts like very high static pressure and makes them less compressible or even non-compressible [44]. Hydration numbers (n_H) of both studied solutes are reported in Table-5. The n_H values for the binary system of (L- lysine·HCl + water) are in good agreement with literature [45].

It is observed (Table-5) that the hydration number (n_H) decreases with increase in temperature of the solution suggesting the extent of cosphere water around the ions decreases with rise in temperature. It may be due to the fact that the system becomes less compressible at higher temperature, so the number of water molecules attached to solute molecules decreases and thus, the hydration number decreases (water-water bonds are broken with increase in temperature). Lowering of n_H with temperature indicates exclusion of some water molecules out of the hydration sphere as a consequence of increased solute-solute interactions. This effect is attributed to the stronger interactions of the amino acids with the water molecules that lead to reduction in the electrostriction of water molecules by the charged end groups.

Conclusion

Positive values of V_ϕ^0 for D(+) glucosamine·HCl + H_2O and L-lysine·HCl + H_2O binary systems indicate the presence of strong solute-solvent interactions and these interactions are strengthened with increase in temperature. Increase in V_ϕ^0 value with rise in temperature for both aqueous binary systems suggest that when the amino acid derivative is transferred to the infinitely dilute solution in water, there could be restructuring of the water molecules near the non-polar residues of the solute molecules. This could be due to the hydrophobic effect in which non-polar substances tend to aggregate in aqueous solution and exclude water molecules. The negative values of (K_ϕ^0) indicate that the water molecules surrounding the amino acid derivatives would present greater resistance to compression than water molecules present in bulk. It is observed that the (K_ϕ^0) values become less negative with rise in temperature. This is expected, as at lower temperature, water around the solute molecule is tightly bound to the solute and yields a high negative value. The more negative values of (K_ϕ^0) for amino acid derivatives at low temperature are attributed to the strong attractive interactions between amino acid derivatives and water. Hydration number decreases with increase in temperature of the solution suggesting the extent of the co-sphere water around the ions decreases with rise in temperature. Also, the positive values of $\partial^2 V_\phi^0/\partial T^2$ and E_ϕ^0 reveal that D(+) glucosamine·HCl and L-lysine·HCl behave as a water structure promoter when dissolved in water.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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