Thermodynamic interactions of l-histidine in aqueous fructose solutions at different temperatures

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Abstract The present experimental investigation has been carried out in order to explore the possible molecular interionic interactions of l-histidine in aqueous fructose solution at 298.15 K, 303.15K, 308.15K, and 313.15 K. Experimental values of density (ρ), ultrasonic speed (u) , and viscosity (η) have been measured on the liquid ternary mixtures of water +fructose + l-histidine and relevant molecular interaction parameters such as the apparent molal volume, V_φ , partial apparent molal volume, V_φ^0 and the slope, S_v, Hepler's constant, $\partial^2 V_\varphi^0/\partial T^2$, apparent molal compressibiliity, K_φ , partial apparent molal compressibility, K_φ^0 and the slope, S_k, transfer volume, $V_{\varphi\ tr}^0$, transfer compressibility, $K_{\varphi\ tr}^0$, Jones–Dole coefficient, B, Jones–Dole coefficient transfer, B_{tr} , temperature derivative of B-coefficient, dB/dT, free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{0*}$ and per mole of solute, $\Delta\mu_2^{0*}$ have been calculated. The results are interpreted in terms of solute–solvent and solute–solute interactions in these systems. It is observed that there exist strong solute–solvent interactions in these systems, which increase with increase in fructose concentration. The thermodynamics of viscous flow has also been discussed.

Index Terms- l-histidine, fructose, adiabatic compressibility, apparent molal volume, B-coefficient

I. INTRODUCTION

Polyhydroxyl compounds play a very important role in stabilizing the native conformations of proteins /enzymes [1–3].Due to the complex nature of these biological macromolecules the stabilization mechanism of proteins and their unfolding behavior in solution is not well understood yet [4].In living organisms, interactions of carbohydrates with proteins play a key role in a wide range of biochemical processes. In particular, carbohydrates, located at cell surfaces, are of importance as receptors with regard to the bioactive structures of hormones, enzymes, viruses, antibodies, etc.[5] Thus, the studies on carbohydrate–protein interactions are very important for the field of immunology, biosynthesis, pharmacology, and medicine. As protein molecules are highly complex systems, amino acids are preferred in molecular interaction studies by several authors instead of proteins. However most of these studies available in literature involves amino acids with non-polar, polar, and uncharged R group with aqueous carbohydrate solutions[6]. However the molecular interaction studies of amino acids with positively charge R group with carbohydrates are scarce. For example Nain et al., [6,7], studied and reported the volumetric, ultrasonic, and viscometric behavior of l-histidine in aqueous glucose solutions , l-histidine in aqueous sucrose solutions, and Zhao et al [8], has reported volumetric and viscometric properties of arginine in aqueous-carbohydrate solutions, . In this report the molecular interaction studies of l-histidine in aqueous fructose solution are reported. L- Histidine is a semi essential amino acid, has positively charged R group and essential in growing children, pregnancy and lactating women . Furthermore, Histamine which is formed by decarboxylation of amino acid 'Histidine', that acts as a neurotransmitter, particularly in the hypothalamus. D-fructose is a ketohexose commonly called as fruit sugar, much sweeter than sucrose and more reactive than glucose. Human seminal fluid is rich in fructose and sperms utilize fructose for energy [9]. These considerations led us to undertake the study of L-histidine (with positively charged R group) in aqueous- fructose solutions. As a part of the continuation of our studies of the thermodynamic properties of amino acids in aqueous salt/drug solutions [10-14], in this paper, experimental results of density, ρ , ultrasonic speed, u, and viscosity, η have been used to calculate the apparent molal volumes, partial apparent molal volumes and the slope, transfer volumes, Hepler's constant , Jones–Dole coefficient, B, and temperature derivative of B-coefficient, dB/dT, the Gibbs free energies of activation of viscous flow per mole of solvent and per mole of solute. These parameters have been used to discuss the solute–solute and solute–solvent interactions in these systems. The thermodynamics of viscous flow has also been discussed.

II. EXPERIMENTAL

Fructose (99% assay, Merck Ltd. Mumbai), L-histidine(99% assay, Loba Chemie Pvt Ltd), havebeen used after drying over P_2O_5 in a desiccators for 72 hrs before use. L-histidine of molality (0.02, 0.04, 0.06, 0.08 and 0.1)M have been used as solutes in four different molal concentration of aqueous fructose solvents, which are prepared using doubly distilled deionized water with a conductivity of 1.5×10^{-4} $\Omega^{-1}\cdot m^{-1}$. The mass measurements have been made using a high precision electronic balance (Model HR 300, Japan) with a precision of ± 0.1 mg.

The densities of the solutions have been measured using a single stem Pycnometer (Pyrex glass) of bulb capacity of 13×10^{-3} dm^3 having graduated stem with 5×10^{-7} dm^3. The reproducibility of density measurements is with ± 2.8×10^{-4} $g\cdot cm^{-3}$. The necessary air buoyancy corrections are also taken care off. The ultrasonic speed has been determined using a ultrasonic interferometer (F-05, Mittal make, India) at a frequency of 2 MHz and the reproducibility of the speed values are within ± 0.03%.

Viscosity has been was measured using a suspended level Ubbelhodde viscometer with a flow time of 466s for doubly distilled deionized water at 303.15 K. Flow times have been measured using a Racer digital stopwatch having an accuracy of ±0.01s. An average of three sets of flow times readings have been taken for each solution for calculation of viscosity. The overall experimental reproducibility is estimated to be within ± 2×10^{-3} m Pa·s. The pycnometer and viscometer filled with test solution have been allowed to stand for about 30 minutes in the thermostatic water bath so as to minimize thermal fluctuations. The temperatures of the solutions have been maintained to an uncertainty of ± 0.01 K in an electronically controlled thermostatic water bath (Eurotherm, Mittal enterprises, New Delhi). These instruments have been initially standardized using doubly distilled deionized water at different temperatures and the measured values of ρ, u and η are found to be in fairly good agreement with the literature values, thus validating our experimental procedures.

III.RESULTS AND DISCUSSSION

The experimental values of density, ρ , ultrasonic speed, u, and viscosity, η of L-histidine solutions in water and in aqueous-fructose solvents as functions of L-histidine concentration and temperature are listed in table 1.

3.1. Apparent molal volume and compressibility

The apparent molal volume, V_φ and apparent molal compressibility, K_φ , of these solutions have been calculated by using the relations

$$V_\varphi = (M/\rho)-1000\,(\rho-\rho_0)/m\,\rho\,\rho_0 \qquad (1)$$

$$K_\varphi = \beta_s M/\rho + 1000\,(\beta_s\,\rho_0 - \beta_0\,\rho)/m\,\rho\,\rho_0 \qquad (2)$$

where m is the molal concentration of the solute (l-histidine), ρ and ρ_0 are the densities of the solution and the solvent (aqueous-fructose), respectively; M is the molal mass of the solute (l-histidine), β_s and β_0 are values of the isentropic compressibility of the solution and the solvent (aqueous- fructose), respectively, calculated using the relation

$$\beta_s = 1/(\rho\,u^2) \qquad (3)$$

The values of V_φ and K_φ as functions of L-histidine concentration and temperature are calculated. It is observed that, linearities between V_φ / K_φ versus m is observed in the studied concentration range and at each investigated temperature. Furthermore it is seen that the values of V_φ increase with increase in concentration of solute as well as temperature, thereby showing the presence of strong solute-solvent interactions. It is further seen that, the K_φ values are negative and increases with increase in concentration and also investigated temperature that may be attributed to the disruption of side group hydration by that of the charged end.

3.2. Partial apparent molal volume and compressibility

The values of partial apparent molal volume, V_φ^0 and the slope, S_v, partial apparent molal compressibility, K_φ^0 and the slope, S_k have been obtained using method of linear regression of V_φ and K_φ vs m curves from the following relations [15]

$$V_\varphi = V_\varphi^0 + S_v\,m \qquad (4)$$

$$K_\varphi = K_\varphi^0 + S_k\,m \qquad (5)$$

where the intercepts, V_φ^0 / K_φ^0, by definition are free from solute–solute interactions and therefore provide a measure of solute–solvent interactions, whereas the experimental slope, S_v / S_k provides information regarding solute–solute interaction. The values of V_φ^0, S_v , K_φ^0 and S_k along with the standard deviations of linear regression, σ for l-histidine in aqueous-fructose solutions at different temperatures are listed in table 2. A perusal of table 2 reveals that the V_φ^0 values are positive and S_v values are negative for l-histidine in aqueous-fructose solutions indicating the presence strong solute– solvent interactions and weak solute–solute interactions in these systems.

The trends observed in V_φ^0 values may be attributed to their hydration behavior [16-21], which comprises of following interactions in these systems: (a) The terminal groups of zwitterions of amino acids, NH_3^+, and COO^-, are hydrated in an electrostatic manner whereas, hydration of R group depends on its nature, which may be hydrophilic, hydrophobic, or amphiphilic; (b) electrostriction of NH_3^+ group is 10 times greater than COO^-group; and (c) the overlap of hydration co-spheres of terminal NH_3^+ and COO^-groups and of adjacent groups results in volume change. The V_φ^0 values increase with increase in concentration of solutes may be related to the reduction in the electrostriction at terminals. The increase in V_φ^0 values (Table 2) with increase in temperature for l-histidine in aqueous-fructose solutions can be explained by considering the size of primary and secondary solvation layers around the zwitterions[6,7,22,23,24,25].

The values of K_φ^0 are negative (Table 2) for l-histidine in aqueous fructose solutions, indicating that the water molecules around ionic charged groups of amino acids are less compressible than the water molecules in the bulk solution [26,27]. This further supports the conclusion that there exist strong solute–solvent interactions and weak solute–solute interactions in these systems.

The values of K_φ^0 are negative and S_k are positive (Table 2) for l-histidine in aqueous fructose solutions, compliments the existence of strong solute–solvent interactions and weak solute–solute interactions in these systems. Furthermore these results concludes that the hydrophilic–ionic groups and hydrophilic–hydrophilic group interactions between OH groups of fructose with zwitterions of l-histidine dominate in these systems[6]. The values of K_φ^0 increase with increase in temperature, indicating release of more water molecules from the secondary solvation layer of l-histidine zwitterions into the bulk, thereby, making the solutions more compressible.

3.3.Transfer volume

Partial apparent molal properties of transfer provide qualitative as well as quantitative information regarding solute–solvent interactions without taking into account the effects of solute–solute interactions [28]. The transfer volumes, $V_{\varphi\,tr}^0$ of l-histidine from water to aqueous-fructose solutions were calculated by using the relation

$$V_{\varphi\,tr}^0 = V_{\varphi\,\text{aq.-fructose}}^0 + V_{\varphi\,\text{water}}^0 \qquad (6)$$

where $V_{\varphi\,\text{water}}^0$ is the partial apparent molal volume of l-histidine in water (Table 2). The $V_{\varphi\,tr}^0$ values for l-histidine from water to aqueous-fructose solutions are included in table 2 and also

represented graphically in Figure1.In general,the types of interactions occurring between l-histidine and fructose can be classified as follows [19,20,29]:

(a) The hydrophilic–ionic interaction between OH groups of fructose and zwitterions of l-histidine.

TABLE 1:Densities, ρ, ultrasonic speeds, u, and viscosities, η of solutions of l-histidine in fructose+water solvents at different temperatures

m /	T/K											
mol·kg^{-1}	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
					l-Histidine in water							
		ρ x10^{-3} / kg· m^{-3}				u / m·s^{-1}				η / m.Pa.s		
0	0.99704	0.99564	0.99402	0.9922	1496.6	1509.4	1520.1	1529.1	0.8905	0.7969	0.719	0.6523
0.02	0.99817	0.99676	0.99513	0.99331	1498.2	1510.9	1521.6	1530.5	0.899	0.8037	0.7236	0.656
0.04	0.9993	0.99789	0.99625	0.99441	1499.7	1512.3	1522.9	1531.7	0.9068	0.8097	0.7284	0.6596
0.06	1.00043	0.99901	0.99737	0.99552	1501.1	1513.6	1524.2	1532.9	0.9143	0.8157	0.7332	0.6633
0.08	1.00157	1.00014	0.99849	0.99664	1502.4	1514.6	1525.4	1533.9	0.9218	0.8217	0.7378	0.6668
0.10	1.0027	1.00127	0.99962	0.99776	1503.8	1515.7	1526.2	1534.7	0.9296	0.8277	0.742	0.6701
					l-Histidine in 0.05 M_S/(mol·kg^{-1}) aqueous fructose							
0	1.00048	0.99902	0.99737	0.99549	1499.7	1512.5	1523.2	1532.2	0.911	0.8146	0.7344	0.6655
0.02	1.00161	1.00014	0.99848	0.99659	1501.3	1514	1524.7	1533.6	0.9199	0.8217	0.7393	0.6694
0.04	1.00274	1.00126	0.9996	0.9977	1502.8	1515.4	1526	1534.8	0.928	0.8279	0.7442	0.6731
0.06	1.00387	1.00239	1.00073	0.99882	1504.2	1516.6	1527.2	1535.8	0.9361	0.834	0.7491	0.6769
0.08	1.00501	1.00353	1.00185	0.99993	1505.5	1517.6	1528.3	1536.7	0.944	0.8405	0.754	0.6805
0.10	1.00616	1.00466	1.00299	1.00107	1506.8	1518.6	1529.1	1537.5	0.952	0.8469	0.7586	0.6841
					l-Histidine in 0.10 M_S/(mol·kg^{-1}) aqueous fructose							
0	1.00389	1.00237	1.00069	0.99875	1502.8	1515.6	1526.3	1535.3	0.931	0.8319	0.7655	0.6791
0.02	1.00501	1.00348	1.0018	0.99985	1504.4	1517.1	1527.8	1536.7	0.9402	0.8392	0.7708	0.6832
0.04	1.00613	1.0046	1.00291	1.00096	1505.8	1518.5	1529.1	1537.9	0.9488	0.8456	0.7761	0.687
0.06	1.00726	1.00573	1.00403	1.00207	1507.2	1519.7	1530.3	1538.9	0.957	0.8523	0.7815	0.6909
0.08	1.00839	1.00686	1.00516	1.0032	1508.6	1520.6	1531	1539.7	0.9654	0.8589	0.7866	0.6947
0.10	1.00952	1.00799	1.0063	1.00434	1509.4	1521.6	1532.1	1540.4	0.9737	0.8653	0.7917	0.6985
					l-Histidine in 0.15 M_S/(mol·kg^{-1}) aqueous fructose							
0	1.00724	1.00563	1.00383	1.00192	1505.8	1518.7	1529.4	1538.4	0.9502	0.8492	0.7655	0.6926
0.02	1.00836	1.00674	1.00493	1.00301	1507.4	1520.2	1530.9	1539.8	0.9597	0.8568	0.7708	0.6968
0.04	1.00948	1.00786	1.00604	1.00412	1508.8	1521.5	1532.2	1541	0.9685	0.8635	0.7761	0.7008
0.06	1.01061	1.00899	1.00717	1.00523	1510.1	1522.7	1533.4	1542	0.9768	0.8703	0.7815	0.7048
0.08	1.01176	1.01012	1.00829	1.00635	1511.3	1523.5	1534.1	1542.7	0.9856	0.8774	0.7866	0.7087
0.10	1.01291	1.01127	1.00943	1.00749	1512.3	1524.2	1535	1543.3	0.9946	0.8839	0.7917	0.7126
					l-Histidine in 0.20 M_S/(mol·kg^{-1}) aqueous fructose							
0	1.01057	1.0089	1.00704	1.0051	1508.7	1521.8	1532.5	1541.5	0.9694	0.866	0.7799	0.706
0.02	1.01168	1.01	1.00814	1.00619	1510.3	1523.3	1534	1542.9	0.9792	0.8739	0.7854	0.7104
0.04	1.0128	1.01112	1.00925	1.00729	1511.5	1524.7	1535.3	1544.1	0.9883	0.8808	0.7908	0.7145
0.06	1.01392	1.01223	1.01036	1.0084	1512.6	1525.8	1536.4	1545.1	0.9972	0.8878	0.7964	0.7186
0.08	1.01505	1.01336	1.01148	1.00951	1513.7	1526.7	1537.2	1545.9	1.0062	0.895	0.8017	0.7227
0.10	1.01619	1.01449	1.01262	1.01064	1514.3	1527.4	1537.8	1546.1	1.0153	0.9021	0.807	0.7267

m, Molality of l-histidine,M_s Molality of fructose

TABLE 2:Partial apparent molal volume, V_φ^0, slope, S_v, transfer volume, $V^0_{\varphi\,tr}$, partial apparent molar compressibility, K_φ^0, slope, S_k, transfer compressibility, $K^0_{\varphi\,tr}$r and standard deviations of linear regression, σ for l-histidine in aqueous fructose solutions at different temperatures.

	T/K				T/K			
Property	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
	l-Histidine in water							
$10^6 .V_\varphi^0$ /(m^3·mol^{-1})	98.900	99.305	99.753	100.336				
	98.860[a]		99.900[a]	100.400[a]				
10 . σ for equation 5	0.075	0.057	0.084	0.021				
$10^6 .S_v$ /(m^3·mol^{-1} kg^{-1})	-7.931	-8.239	-8.397	-9.677				
$10^{15}. K_\varphi^0$ /(m^3 ·mol^{-1}· Pa^{-1})	-3.013	-2.721	-2.582	-2.224				
	-2.96[b]		-2.59[b]					
σ for equation 6	0.069	0.075	0.1	0.074				
$10^{18}. S_k$ /(kg.m^3. N^{-1}·mol^{-2}· Pa^{-1})	5.857	8.717	8.608	8.706				
	l-Histidine in 0.05 / 0.10 M_S/(mol·kg^{-1}) aqueous fructose							
$10^6 .V_\varphi^0$ /(m^3·mol^{-1})	99.028	99.423	99.859	100.433	99.155	99.539	99.964	100.529
10 . σ for equation 5	0.039	0.049	0.048	0.1	0.046	0.053	0.027	0.05
$10^6 .S_v$ /(m^3·mol^{-1} kg^{-1})	12.068	-12.16	-13.531	-14.152	10.477	12.666	-14.797	-17.348
$10^6 .V^0_{\varphi\,tr}$ /(m^3·mol^{-1})	0.128	0.118	0.106	0.097	0.255	0.234	0.211	0.193
$10^{15}. K_\varphi^0$ /(m^3 ·mol^{-1}· Pa^{-1})	-2.95	-2.676	-2.551	-2.205	-2.893	-2.633	-2.524	-2.191
σ for equation 6	0.04	0.058	0.044	0.06	0.016	0.011	0.014	0.04
$10^{18}. S_k$ /(kg.m^3. N^{-1}·mol^{-2}· Pa^{-1})	5.937	9.766	10.03	10.893	8.212	10.687	11.564	12.029
$10^{15}. K^0_{\varphi\,tr}$ /(m^5 N^{-1}·mol^{-1})	0.063	0.045	0.031	0.019	0.12	0.088	0.058	0.033
	l-Histidine in 0.10 / 0.20 M_S/(mol·kg^{-1}) aqueous fructose							
$10^6 .V_\varphi^0$ /(m^3·mol^{-1})	99.28	99.654	100.068	100.624	99.404	99.769	100.169	100.717
10 . σ for equation 5	0.035	0.065	0.056	0.035	0.03	0.064	0.046	0.01
$10^6 .S_v$ /(m^3·mol^{-1} kg^{-1})	16.723	16.573	-15.975	-17.388	14.385	14.625	-17.828	-17.278
$10^6 .V^0_{\varphi\,tr}$ /(m^3·mol^{-1})	0.38	0.349	0.315	0.288	0.504	0.464	0.416	0.381
$10^{15}. K_\varphi^0$ /(m^3 ·mol^{-1}· Pa^{-1})	-2.837	-2.594	-2.499	-2.177	-2.783	-2.561	-2.478	-2.168
σ for equation 6	0.06	0.08	0.05	0.11	0.019	0.1	0.05	0.11
$10^{18}. S_k$ /(kg.m^3. N^{-1}·mol^{-2}· Pa^{-1})	9.136	12.943	12.483	13.363	14.76	12.761	13.982	14.373
$10^{15}. K^0_{\varphi\,tr}$ /(m^5 N^{-1}·mol^{-1})	0.176	0.127	0.083	0.047	0.23	0.16	0.104	0.056

[a] Reference [30]; [b] Reference [31]

(b) Hydrophilic–hydrophilic interaction the OH groups of fructose and NH groups in the side chain of acid l-histidine mediated through hydrogen bonding.

(c) Hydrophilic–hydrophobic interaction between the OH groups of fructose molecule and non-polar (−CH2) in the side chain of l-histidine molecule.

(d) Hydrophobic–hydrophobic group interactions between the non-polar groups of fructose and non-polar (−CH2) in the side chain of l-histidine molecule.

Generally the values of $V^0_{\varphi\,tr}$ increase due to reduction in the electrostriction at terminals by positive contribution from the interactions of type (a) and (b), whereas it decreases due to disruption of side group hydration by that of the charged end by negative contribution from the interactions of type (c) and (d) mentioned earlier. The observed positive $V^0_{\varphi\,tr}$ values in this work suggest that the hydrophilic–ionic group and hydrophilic–hydrophilic group interactions dominate in the studied systems. [6,7,32]

3.4.Transfer Compressibilty

The transfer compressibility of l-histidine from water to aqueous fructose solutions, $K^0_{\varphi\,tr}$ were calculated by the following relation

$$K^0_{\varphi\,tr} = K^0_{\varphi\,aq.\text{-}fructose} + K^0_{\varphi\,water} \quad (7)$$

where $K^0_{\varphi\,water}$ is the partial apparent molal volume of l-histidine in water (Table 2). The $K^0_{\varphi\,tr}$ values for l-histidine from water to aqueous-fructose solutions are included in Table 2 and also represented graphically in Figure 2. The observed positive $K^0_{\varphi\,tr}$

values suggest that the hydrophilic– ionic groups and hydrophilic–hydrophilic group interactions dominate in these systems. The $K^0_{\varphi tr}$values increase with increase in fructose concentration in the solutions (Fig. 2). This may be due to greater

TABLE 3:Jones–Dole coefficient, B and standard deviations of linear regression, σ , Gibbs energies of activation of viscous flow per mole of solvent, $\Delta\mu_1^{0*}$, and per mole of solute, $\Delta\mu_2^{0*}$ for l-histidine in aqueous fructose solutions at different temperatures.

	T/K				T/K			
Property	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
			l-Histidine in water					
10^3.B /(m^3·mol^{-1})	0.434	0.382	0.327	0.276				
	0.436[c]	0.384[c]	0.329[c]	0.276[c]				
σ for equation 5	0.021	0.005	0.047	0.03				
$\Delta\mu_1^{0*}$/ (kJ·mol^{-1})	9.16	9.04	8.93	8.83				
$\Delta\mu_2^{0*}$/ (kJ·mol^{-1})	79.8	73.57	66.7	60.19				
			l-Histidine in 0.05 / 0.10 M_S/(mol·kg^{-1}) aqueous fructose					
10^3.B /(m^3·mol^{-1})	0.445	0.391	0.334	0.281	0.452	0.397	0.339	0.285
σ for equation 5	0.008	0.003	0.002	0.015	0.015	0.018	0.03	0.007
$\Delta B .10^3$ / (m^3·mol^{-1})	0.011	0.009	0.007	0.005	0.018	0.015	0.012	0.009
$\Delta\mu_1^{0*}$/ (kJ·mol^{-1})	9.23	9.11	9.00	8.89	9.30	9.17	9.06	8.96
$\Delta\mu_2^{0*}$/ (kJ·mol^{-1})	81.05	74.59	67.48	60.73	81.74	75.18	67.98	61.12
			l-Histidine in 0.10 / 0.20 M_S/(mol·kg^{-1}) aqueous fructose					
10^3.B /(m^3·mol^{-1})	0.459	0.403	0.344	0.288	0.465	0.408	0.348	0.29
σ for equation 5	0.039	0.028	0.021	0.008	0.013	0.024	0.017	0.005
$\Delta B .10^3$ / (m^3·mol^{-1})	0.025	0.021	0.017	0.012	0.031	0.026	0.021	0.014
$\Delta\mu_1^{0*}$/ (kJ·mol^{-1})	9.36	9.24	9.13	9.02	9.42	9.30	9.19	9.08
$\Delta\mu_2^{0*}$/ (kJ·mol^{-1})	82.43	75.77	68.46	61.36	82.97	76.21	68.8	61.46

[c] Reference[6]

hydrophilic–ionic group and hydrophilic– hydrophilic group interactions with increased concentrations of fructose. The observed trends in K_φ^0 and $K_{\varphi\,tr}^0$ further support the conclusions drawn from V_φ^0 and $V_{\varphi\,tr}^0$. The decrease in $V_{\varphi\,tr}^0$ and $K_{\varphi\,tr}^0$ values with increase in temperature however indicate that release of water molecules from the secondary solvation layer of l-histidine zwitterions into the bulk, becomes difficult with addition of fructose in the solution due to greater hydrophilic–ionic groups and hydrophilic– hydrophilic group interactions as compared to those in water.

3.5. Hepler's constant

Hepler [33]devised a method to account the structure making / breaking properties of solutes in aqueous solutions using the sign of $(\partial^2 V_\varphi^0/\partial T^2)$. On the basis of this criteria, a structure making solute will exhibit positive $(\partial^2 V_\varphi^0/\partial T^2)$ values and structure breaking solute will show negative $(\partial^2 V_\varphi^0/\partial T^2)$ values [34].The values of Hepler's constant are given in Table 4. The positive values of $(\partial^2 V_\varphi^0/\partial T^2)_p$ in table 4 indicates that l-histidine act as structure-maker in aqueous-fructose solvents.

3.6. Analysis of viscosity data

The viscosity data were analysed by using Jones–Dole [35] equation of the form

$$\eta_r = \eta / \eta_0 = 1 + B\cdot c \qquad (8)$$

where η_r is the relative viscosity of the solution, η and η_o are the viscosities of solution and the solvent (fructose+water), respectively, m is molality of l-histidine in fructose+water solvent, B is the Jones–Dole coefficients and , c, is the molarity (calculated from molality data), respectively. The values of B along with the standard deviations of linear regression, σ are listed in Table 3. B- Coefficient is a measure of structural modifications induced by the solute–solvent interactions [36,37] . The values B-coefficients are positive, suggesting weak solute–solute and strong solute–solvent interactions in these solutions. [6].Furthermore B-coefficients increase (Fig. 3) with increasing concentration of fructose, the reason may be that the friction increases to prevent water flow at increased fructose concentration. Thus, the values of B-coefficient support the behaviors of V_φ^0 , K_φ^0 , S_v, S_k, $V_{\varphi\,tr}^0$ and $K_{\varphi\,tr}^0$, which suggest stronger solute–solvent interactions as compared to solute–solute interactions in studied ternary solutions. The temperature derivatives of B-coefficient (dB/dT) have also been calculated and included in the Table 4. In general, the dB/dT is negative for structure-maker and positive for structure-breaker solutes in

TABLE 4:Hepler's constant, $\partial^2 V_\varphi^0/\partial T^2$ and temperature derivative of B-coefficient, dB/dT for l-histidine in aqueous Fructose solutionsat different temperatures.

0.05 M_S/	$\partial^2 V_\varphi^0/\partial T^2$ /	dB/dT /
($mol \cdot kg^{-1}$)	($m^6 . mol^{-2} \cdot k^{-2}$)	($m^3 \cdot mol^{-1} \cdot K^{-1}$)
0	0.00178	-0.0106
0.05	0.00179	-0.011
0.1	0.00181	-0.0112
0.15	0.00182	-0.0114
0.2	0.00183	-0.0117

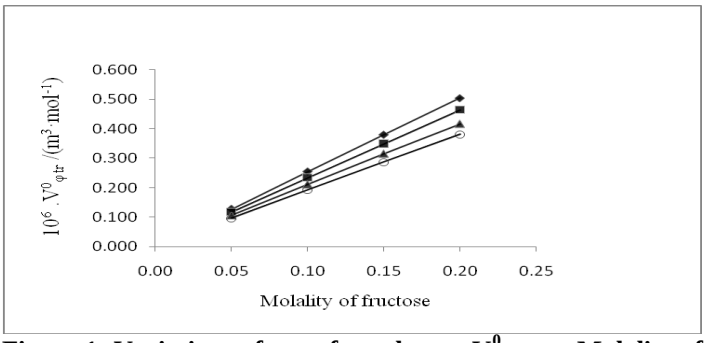

Figure 1: Variations of transfer volume , $V^0_{\varphi\,tr}$ vs. Molality of fructose, M_s, for l-histidine in fructose+ water solutions at temperatures, T/K=298.15, ♦; T/ K=303.15, ■; T/K=308.15, ▲; T/K=313.15, ○.

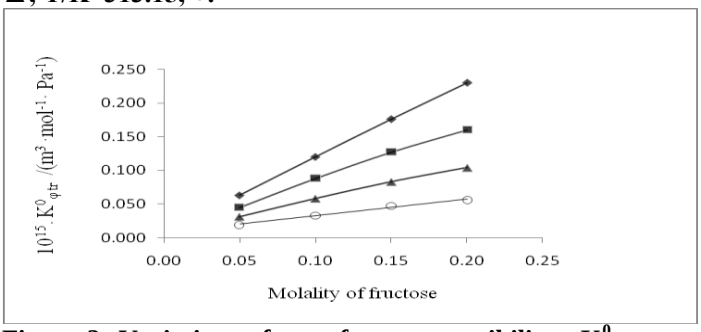

Figure 2: Variations of transfer compressibility , $K^0_{\varphi\,tr}$ vs. Molality of fructose, M_s, for l-histidine in fructose+ water solutions at temperatures, T/K=298.15, ♦; T/ K=303.15, ■; T/K=308.15, ▲; T/K=313.15, ○.

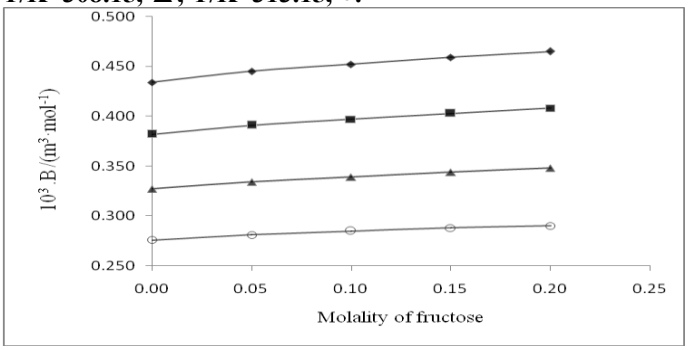

Figure 3:Variations of Jones-Dole coefficient, B vs. Molality of fructose, M_s, for l-histidine in fructose+ water solutions at temperatures, T/K=298.15, ♦; T/ K=303.15, ■; T/K=308.15, ▲; T/K=313.15, ○.

solution[38]. The negative dB/dT values for l-histidine in aqueous-fructose solvents (see table 6) indicate that l-histidine act as structure-maker in aqueous-fructose solvents under study[24,39,40].

3.7. Thermodynamics of viscous flow

The viscosity data are used to estimate the free energy of activation per mole of the solvent ($\Delta\mu_1^{0*}$) and solute ($\Delta\mu_2^{0*}$) as suggested by Feakins et al. [41] and Eyring et al.[42] from Eqns. (9),(10) and (11)

$$B = (\bar{V}_1^0 - \bar{V}_2^0)/1000 + \bar{V}_1^0/1000RT(\Delta\mu_2^{0*} - \Delta\mu_1^{0*}) \quad (9)$$

$$\Delta\mu_1^{0*} = RT\ln(\eta_0\bar{V}_1^0/hN) \quad (10)$$

Equation (10) can be rearranged as

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + RT/\bar{V}_1^0[1000B - (\bar{V}_1^0 - \bar{V}_2^0)] \quad (11)$$

It is evident from table 3 that for l-histidine in aqueous-fructose solutions, the $\Delta\mu_2^{0*}$ values are positive and much larger than those of $\Delta\mu_1^{0*}$ in aqueous-fructose solvents. This suggests that the process of viscous flow becomes difficult as the temperature and molality increases. Hence, the formation of transition state becomes less favourable. According to Feakins et al.[36,41] and Glasstone et al.[42] , $\Delta\mu_2^{0*} > \Delta\mu_1^{0*}$ for solutes with positive viscosity B-coefficients indicates stronger solute–solvent interactions in the ground state than in the transition state, i.e., the formation of a transition state is accompanied by the rupture and distortion of the intermolecular forces in the solvent structure. Thus, the conclusions drawn from $\Delta\mu_2^{0*}$ are in agreement with those drawn from the trends of V_φ^0 , $V^0_{\varphi\,tr}$, K_φ^0 , $K^0_{\varphi\,tr}$ and B values

IV. CONCLUSION

The densities, ρ, ultrasonic speeds, u, and viscosities, η of solutions of l-histidine in aqueous-fructose solvents of molalities (0.05,0.10,0.15,0.20)M_s were measured at different temperatures. From the experimental data, various parameters, viz., Vϕ, V_φ^0 , $V_\varphi^{0,} K_\varphi^0$, $V^0_{\varphi\,tr}$, $K^0_{\varphi\,tr}$, Jones–Dole coefficient, B and dB/dT were calculated. The results indicate that there exist strong solute–solvent (hydrophilic–ionic group and hydrophilic–hydrophilic group) interactions in these systems, which increase with increase in fructose concentration. It is also observed that l-histidine acts as structure-maker in these aqueous-fructose solvents.

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