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Studies on volumetric and viscometric properties of l-histidine in aqueous xylose solution over temperature range (298.15 to 313.15) K.

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Abstract: Density and Viscosity measurement have been performed for L-histidine in aqueous Xylose (0.05,0.01,0.15,0.20)M at 298.15,303.15,308.15 and 313.15k. The measured values of density and viscosity have been used to estimate some important parameters such as the apparent molal volume, partial molal volume, the partial molal volume transfer, partial molal expansivity, isobaric thermal expansion coefficients, Viscosity B-Coefficients, B-Coefficient transfer, Ratio of B Coefficient to partial molal volume, temperature derivative of B-coefficient, free energy of activation of viscous flow per mole of solvent and per mole of solute and thermodynamic activation parameter of transfer from ground state to transition state of L-histidine in aqueous Xylose solution. These parameters are inspected in terms of solute-solute and solute-solvent interactions and structure making / breaking ability of solute in the solvent.
Keywords: Partial molal volume, B-Coefficients, Partial molal volume transfer, B-Coefficient transfer.

Introduction:

Saccharides and their derivatives are widely distributed in various forms of life as essential moieties of glycoproteins, glycolipids, nucleic acids and polysaccharides. These are found with an enormous range of complexity, from simple mono- to mega-dalton polysaccharide structures. Because of conformational flexibility, saccharides play significant roles in many biological processes such as signaling, cell-cell recognition, molecular and cellular communication[1,2,3,4.] The studies on carbohydrate–protein interactions are very important for the field of immunology, biosynthesis, pharmacology, and medicine. In living organisms, interactions of saccharides with model molecules of proteins play a key role in understanding the thermodynamic behavior of biochemical process in the body system. To understand mechanisms of biological processes, low molecular model compounds (e.g. alcohols, saccharides, peptides, nucleic acid bases, nucleosides and nucleotides) have been studied due to the complexities of biomolecules. Saccharides are important compounds due to their hydrophilic hydroxy (–OH) rich periphery, coordinating ability, homochirality, stereospecificity, etc. However, the understanding of the relationship between saccharide structure and their biological function is still far behind that of proteins and nucleic acids [2, 5]. As protein molecules are highly complex systems, amino acids are preferred in molecular interaction studies by several authors instead of proteins. Furthermore 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 xylose 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- Xylose is an essential sugar saccharide of the pentose, widely distributed in plants and freely soluble in water.In medicine, xylose is used solely as one of the diagnostic measures for evaluating intestinal absorption and for the diagnosis of malabsorptive states. In addition to that , xylose is an antibacterial, antifungal carbohydrate and vital to cellular communication. Research has given us evidence that xylose may help prevent cancer of the digestive tract [9, 10]. These considerations led us to undertake the study of L-histidine (with positively charged R group) in aqueous- xylose solutions. As a part of the continuation of our studies of the thermodynamic properties of amino acids in aqueous salt/drug solutions[11-19], in this paper, experimental results of density, ρ , and viscosity, η have been used to calculate the apparent molal volume, V_φ partial molal volume, V_φ^0, the partial molal volume transfer, $V_{\varphi\,tr,}^0$ partial molal expansivity, E_2^0,isobaric thermal expansion coefficients, α_2,Viscosity B Coefficients, B-Coefficient transfer, ΔB_{tr}, Ratio of B Coefficient to partial molal volume,(B/V_φ^0), 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, $\Delta\mu_2^{0*}$, and thermodynamic activation parameter of transfer ΔG_2° $(1\rightarrow 1')$] from ground state to transition state of L-histidine in aqueous Xylose solution. These parameters are inspected in terms of solute-solute and solute-solvent interactions and structure making / breaking ability of solute in the solvent.

Experimental:

Xylose (mass fraction purity > 0.990) was procured from S.D. Fine. Chem. Ltd. Mumbai, L-histidine (99% assay, Loba Chemie Pvt Ltd), have been 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 xylose 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 $\pm 2.8\times10^{-4}$ $g\cdot cm^{-3}$. The necessary air buoyancy corrections are also taken care off.[13]

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) [16].

Results:

The apparent molal volume , V_φ of L-histidine in aqueous Xylose solution has been calculated from density (Table-1) by using the relation,

Table 1. Densities, ρ, and viscosities, η, of solutions of l-histidine in xylose +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**
	ρ x10^{-3} / kg· m^{-3}				**η / m.Pa.s**			
	l-Histidine in water							
0	0.99704	0.99564	0.99402	0.99220	0.8905	0.7969	0.7190	0.6523
0.02	0.99817	0.99676	0.99513	0.99331	0.8990	0.8037	0.7236	0.6560
0.04	0.99930	0.99789	0.99625	0.99441	0.9068	0.8097	0.7284	0.6596
0.06	1.00043	0.99901	0.99737	0.99552	0.9143	0.8157	0.7332	0.6633

0.08	1.00157	1.00014	0.99849	0.99664	0.9218	0.8217	0.7378	0.6668
0.1	1.00270	1.00127	0.99962	0.99776	0.9296	0.8277	0.7420	0.6701
	l-Histidine in 0.05 Ms/(mol·kg^{-1}) aqueous xylose							
0	0.99976	0.99834	0.99670	0.99486	0.9054	0.8095	0.7300	0.6631
0.02	1.00088	0.99945	0.99780	0.99595	0.9142	0.8165	0.7349	0.6670
0.04	1.00199	1.00055	0.99889	0.99702	0.9221	0.8228	0.7399	0.6709
0.06	1.00309	1.00163	0.99996	0.99808	0.9299	0.8291	0.7449	0.6746
0.08	1.00419	1.00270	1.00101	0.99912	0.9377	0.8353	0.7497	0.6785
0.1	1.00526	1.00376	1.00205	1.00013	0.9458	0.8415	0.7545	0.6823
	l-Histidine in 0.10 Ms/(mol·kg^{-1}) aqueous xylose							
0	1.00245	1.00100	0.99934	0.99747	0.9212	0.8235	0.7426	0.6729
0.02	1.00356	1.00210	1.00043	0.99855	0.9302	0.8308	0.7477	0.6771
0.04	1.00465	1.00318	1.00150	0.99962	0.9383	0.8372	0.7529	0.6810
0.06	1.00571	1.00424	1.00253	1.00065	0.9464	0.8437	0.7581	0.6851
0.08	1.00676	1.00526	1.00353	1.00164	0.9546	0.8503	0.7634	0.6892
0.1	1.00777	1.00625	1.00451	1.00264	0.9627	0.8568	0.7681	0.6932
	l-Histidine in 0.15 Ms/(mol·kg^{-1}) aqueous xylose							
0	1.00511	1.00363	1.00193	1.00005	0.9352	0.8363	0.7539	0.6833
0.02	1.00621	1.00473	1.00302	1.00113	0.9445	0.8440	0.7593	0.6877
0.04	1.00729	1.00578	1.00408	1.00218	0.9527	0.8506	0.7646	0.6918
0.06	1.00832	1.00684	1.00513	1.00322	0.9611	0.8574	0.7703	0.6962
0.08	1.00932	1.00784	1.00613	1.00421	0.9696	0.8641	0.7754	0.7005
0.1	1.01029	1.00881	1.00711	1.00519	0.9779	0.8710	0.7807	0.7046
	l-Histidine in 0.20 Ms/(mol·kg^{-1}) aqueous xylose							
0	1.00774	1.00622	1.00448	1.00258	0.9495	0.8480	0.7640	0.6932
0.02	1.00884	1.00731	1.00556	1.00365	0.9590	0.8560	0.7697	0.6977
0.04	1.00990	1.00838	1.00662	1.00471	0.9675	0.8628	0.7751	0.7020
0.06	1.01093	1.00941	1.00764	1.00573	0.9762	0.8697	0.7809	0.7066
0.08	1.01194	1.01041	1.00860	1.00668	0.9848	0.8768	0.7864	0.7111
0.1	1.01288	1.01136	1.00956	1.00766	0.9934	0.8839	0.7919	0.7154

$V_\varphi = (M/\rho)\text{-}1000\ (\rho - \rho_0)\ /m\ \rho\ \rho_0$ (1)

Where M is the molar mass of the solute ,m is the molality of solute (L-histidine) ρ and ρ_0 are the densities of the solution and the solvent(aqueous xylose) respectivelty.

The values of partial molal volume , V_φ^0 and the slope ,S_v have been evaluated by least squares fitting of V_φ verses m from the following equation [20],

$V_\varphi = V_\varphi^0 + S_v\, m$ (2)

Where V_φ^0 is the infinite dilution value that is equal to the partial molal property at infinite dilution and S_v is the experimental slope. The V_φ^0 values of L-histidine in water at the studied temperatures agree fairly well with literature values [21] (see table 2) thus validating our experimental procedures .

The partial molal volumes of transfer at infinite dilution of l-histidine from water to aqueous xylose solutions has been calculated using the following relation

$V_{\varphi\ tr}^0 = V_{\varphi\ \text{in aq.-xylose}}^0 - V_{\varphi\ \text{in water}}^0$ (3)

Where $V_{\varphi\ \text{water}}^0$ is the partial molal volume of l-histidine in water (Table-2). The values of $V_{\varphi\ tr}^0$ of l- histidine in water to aqueous xylose solution are included along with standard deviation of linear regression, σ in table 2 and are graphically represented in figure 1.

The values of partial molar expansivity are calculated [22] from the partial molal volume using the relation (4) as follows. These values are included in table (3).

$E_2^0 = (\partial V_\varphi^0/\partial T)_P$ (4)

The values of isobaric thermal expansion coefficients (α_2) of the solute at infinite dilution [23] are also determined from V_φ^0 using the following equation (5) is tabulated in table 2.

$\alpha_2 = (1/V_\varphi^0)(\partial V_\varphi^0/\partial T)_P = E_2^0/V_\varphi^0$ (5)

Table -2 Partial molal volume V_φ^0 and Transfer volumes $V^0_{\varphi\,tr}$ *isobaric thermal* expansion coefficient,α_2, Viscosity *B* coefficients, *B*,and transfer *B* coefficients, ΔB, Ratio of *B* coefficient to partial molal volume, B/V_φ^0, free energy of activation of solvent, $\Delta\mu_1^{0*}$, free energy of activation of solute, $\Delta\mu_2^{0}$*, and thermodynamic activation parameter of transfer, ΔG_2^0 (1→1') from ground state to transition state, and standard deviations of linear regression, σ for l-histidine in aqueous xylose solution 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				*Literature values of l-Histidine in water*			
$10^6 .V_\varphi^0$ /(m^3·mol^{-1})	98.900	99.305	99.753	100.336	98.860[21]		99.900[21]	100.400[21]
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				
$10^4\alpha_2$ / K^{-1}	9.616	9.577	9.534	9.478				
$10^3 .B$ /(m^3·mol^{-1})	0.434	0.382	0.327	0.276	0.436[27]	0.384[27]	0.329[27]	0.276[27]
σ for equation 5	0.021	0.005	0.047	0.030				
B/V_φ^0	4.39	3.85	3.28	2.75				
$\Delta\mu_1^{0*}$/ (kJ·mol^{-1})	9.16	9.04	8.93	8.83				
$\Delta\mu_2^{0*}$/ (kJ·mol^{-1})	79.80	73.57	66.70	60.19				
ΔG^0_2(1→1') / (kJ·mol-1)	70.63	64.53	57.77	51.36				
$10^6 .V_\varphi^0$ /(m^3·mol^{-1})	98.930	99.367	99.848	100.460	98.951	99.386	99.868	100.488
10 . σ for equation 5	0.096	0.067	0.103	0.102	0.096	0.193	0.156	0.302
$10^6 .S_v$ /(m^3·mol^{-1} kg^{-1})	6.415	11.372	14.092	16.588	23.140	25.868	30.888	25.981
$10^6 .V^0_{\varphi\,tr}$ /(m^3·mol^{-1})	0.030	0.062	0.095	0.124	0.051	0.081	0.115	0.152
$10^4\alpha_2$ / K^{-1}	10.209	10.164	10.115	10.054	10.308	10.263	10.213	10.150
$10^3 .B$ /(m^3·mol^{-1})	0.440	0.391	0.340	0.292	0.445	0.399	0.349	0.304
σ for equation 5	0.021	0.005	0.017	0.013	0.010	0.016	0.037	0.017
$\Delta B .10^3$ / (m^3·mol^{-1})	0.006	0.009	0.013	0.017	0.011	0.017	0.022	0.028
B/V_φ^0	4.45	3.93	3.41	2.91	4.50	4.01	3.49	3.03
$\Delta\mu_1^{0*}$/ (kJ·mol^{-1})	9.21	9.09	8.98	8.88	9.27	9.14	9.03	8.93
$\Delta\mu_2^{0*}$/ (kJ·mol^{-1})	80.39	74.62	68.36	62.34	80.85	75.52	69.44	63.88
ΔG^0_2(1→1') / (kJ·mol-1)	71.18	65.53	59.38	53.46	71.58	66.37	60.40	54.95
$10^6 .V_\varphi^0$ /(m^3·mol^{-1})	98.965	99.402	99.896	100.521	98.992	99.442	99.937	100.554
10 . σ for equation 5	0.218	0.373	0.173	26.979	0.183	0.236	0.305	0.458
$10^6 .S_v$ /(m^3·mol^{-1} kg^{-1})	35.715	32.095	27.848	0.159	37.633	33.428	36.437	31.604
$10^6 .V^0_{\varphi\,tr}$ /(m^3·mol^{-1})	0.065	0.097	0.143	0.185	0.092	0.137	0.184	0.218
$10^4\alpha_2$ / K^{-1}	10.408	10.362	10.311	10.247	10.506	10.458	10.407	10.343
$10^3 .B$ /(m^3·mol^{-1})	0.450	0.406	0.358	0.314	0.455	0.413	0.367	0.324
σ for equation 5	0.160	0.240	0.310	0.380	0.012	0.029	0.021	0.022
$\Delta B .10^3$ / (m^3·mol^{-1})	0.016	0.024	0.031	0.038	0.021	0.031	0.040	0.048
B/V_φ^0	4.55	4.08	3.58	3.12	4.60	4.15	3.67	3.22
$\Delta\mu_1^{0*}$/ (kJ·mol^{-1})	9.31	9.19	9.08	8.98	9.36	9.24	9.13	9.03
$\Delta\mu_2^{0*}$/ (kJ·mol^{-1})	81.29	76.27	70.50	65.13	81.73	77.01	71.56	66.36
ΔG^0_2(1→1') / (kJ·mol-1)	71.98	67.07	61.42	56.15	72.37	67.77	62.43	57.34

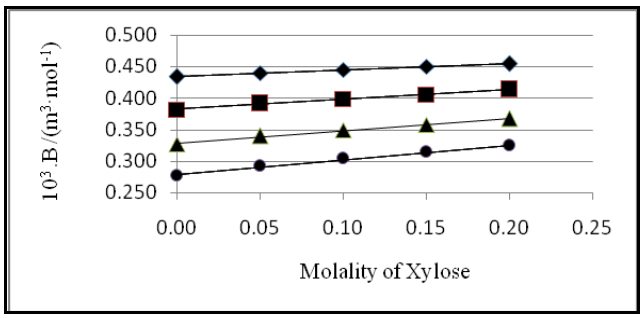

Figure 1. Variations of transfer volume , $V^0_{\varphi\,tr}$ vs. Molality of xylose, M_s, for l-histidine in xylose+ water solutions at temperatures, T/K=298.15, ♦; T/ K=303.15, ■; T/K=308.15, ▲; T/K=313.15, ●

The temperature dependence of V_φ^0 [24] for l-histidine in aqueous xylose solution can be expressed by the equation(6).

$$V_\varphi^0 = a + bT + cT^2 \quad (6)$$

Where a,b and c may be estimated by the least squares fitting of partial molal volume in the above equation. The values, called Hepler's constant [25] gives the information about the structure making / breaking properties of solute in aqueous Xylose solution. On the basis of these criteria, a structure making solute will exhibit positive ($\partial^2V_\varphi^0/\partial T^2$) values and structure breaking solute will show negative ($\partial^2V_\varphi^0/\partial T^2$) values. The values of Hepler's constant are given in table 3.

Table- 3 Partial molar expansivity E_2^0, Temperature derivative of B-coefficient, dB/dT, and Hepler's constants ($\partial_2V_\varphi^0/\partial T^2$), of l-histidine in aqueous xylose solution at different temperatures.

M_S/ (mol·kg^{-1})	10^6 E_2^0/ (m^3·mol^{-1}·K^{-1})	$\partial^2V_\varphi^0/\partial T^2$ / (m^6. mol^{-2}· k^{-2})	dB/dT / (m^3·mol^{-1}·K^{-1})
0.00	0.095	0.00178	-0.0106
0.05	0.101	0.00175	-0.0099
0.10	0.102	0.00185	-0.0095
0.15	0.103	0.00188	-0.0091
0.20	0.104	0.00167	-0.0088

The B-Coefficients data has been evaluated by fitting the values to the Jones-Dole equation by a least squares method [26] as follows.

$$\eta_r = \eta / \eta_0 = 1 + B\cdot c \quad (7)$$

where η_r is the relative viscosity of the solution, η and η_o are the viscosities of solution and the solvent (xylose+water) respectively. m is the molality of l-histidine in aqueous xylose solution , B is the Jones–Dole coefficients and , c is the molarity (calculated from molality data), respectively. The values of B-Coefficients l-histidine in water at the studied temperatures along with the standard derivations of linear regression, σ are listed in table-2 agree fairly well with literature values, thus validating experimental procedures 27.The temperature derivative of B Coefficient (dB/dT) have also been calculated and included in the table.3

The ratio of viscosity B-Coefficients and partial molar volume V_φ^0 ,ie., B /V_φ^0 can be used to judge the solvation of any solute and these values are listed in Table-2.

The viscosity B-coefficients of transfer, ΔB_{tr} of l-histidine from water to aqueous xylose solutions has been calculated using the following relation

$$\Delta B_{tr} = B_{\text{in aq.-xylose}} - B_{\text{in water}} \quad (8)$$

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.[28] and Eyring et al. [29] from Eqns. (9),(10) and (11)

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

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

Equation (10) can be rearranged as

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

Where $\overline{V}_1^{\,0} = (\Sigma x_i m_i / \rho)$ is the mean value of the solvent and $\overline{V}_2^{\,0} = V_\phi^0$ is the partial molal volume at infinite dilution of the solute, h is Plank's Constant ,N_A is avogadro's number , η_o is the viscosity of the solvent and R is the gas constant. The calculated values of $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ are also given in table-2. The activation free energy $\Delta\mu_2^{0*}$ includes the free energy of transfer of solute from ground state to transition solvents [$\Delta G_2°$ (1→1')] and the free energy of solute through its own viscous transition state [$\Delta G_2°$(2→2')].The values of [$\Delta G_2°$(1→1')] may be calculated using $\Delta\mu_2^{0*}$- {[$\Delta G_2°$ (2→2')] = $\Delta\mu_1^{0*}$} similar to the methods reported elsewhere[28,30].These values are given in Table 2.

Thermodynamic transfer functions of amino acids may be expressed by the Mc Millan-Mayer theory of solutions [31, 32] which permits the formal separation of the effects due to the interaction between the pairs of the solute molecules and those due to interactions between three or more molecules by the equation (12) and (13).

$$V^0_{\varphi\,tr\ (water\ to\ aqueous\ xylose\ solution)} = 2V_{AB}\,m_B + 3V_{ABB}\,m_B^{\,2} + \text{----} \qquad (12)$$

$$\Delta B_{tr\ (water\ to\ aqueous\ xylose\ solution)} = 2\eta_{AB}\,m_B + 3\,\eta_{ABB}\,m_B^{\,2} + \text{----} \qquad (13)$$

When A stands for l-histidine and B stands for xylose and m_B is the molality of xylosein water (cosolute).The constants V_{AB} / η_{AB} ,V_{ABB} / η_{ABB} are pair and triplet volumetric/viscometric interaction parameters are obtained by fitting and data to equation (12) &(13).The evaluated parameters V_{AB} / η_{AB} ,V_{ABB} / η_{ABB} for volumes and viscosities are summarized in Table 4.

Table- 4 Values of pair (V_{AB}, η_{AB}) and triplet (V_{ABB}, η_{ABB}) of l-histidine in aqueous xylose solution at different temperatures.

T/K	V_{AB} x10^6 /	V_{ABB} x10^6 /	10^3 η_{AB}/	10^3 η_{ABB}/
	$m^3 \cdot mol^{-2} \cdot kg$	$m^3 \cdot mol^{-3} \cdot kg^2$	$m^3 \cdot mol^{-2} \cdot kg$	$m^3 \cdot mol^{-3} \cdot kg^2$
	From volume		From viscosity	
298.15	0.313	-0.331	0.061	-0.032
303.15	0.651	-1.219	0.094	-0.057
308.15	1.008	-2.091	0.135	-0.129
313.15	1.348	-2.971	0.180	-0.218

Discussion:

On volumetric data:

It is seen from Table- 1 that density of the ternary system increases with increase in concentration solute as well as temperature .This may be attributed to the shrinkage in the volume thereby showing the presence strong solvent interactions. In other words, the increase in density may be interpreted due to the enhanced structure of solvent mixture due to the added solute (l-histidine) [33].

A perusal of table 2 reveals that the V_φ^0 values are positive and S_v values are negative 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, 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 may be attributed to the solvation effect of l-histidine zwitterions in the solvent [6, 7, 34, 35, 36, and 37].

The values of partial molar expansivity E_2^0 is considered to be an important and sensitive indicator of solute-solvent interactions and the structure making or breaking properties of solute. Positive values of E_2^0 (see table 3) indicates that the studied amino acid(l-histidine) is a structure maker in aqueous xylose solvent[38].Furthermore , the values of isobaric thermal expansion coefficient (α_2) for the system investigated (see table 2) are found to decrease with increase in temperature showing the significance of solvent hydroxyl group interactions in the reported systems [39].

The positive values of (Table3) of second derivatives of V_φ^0 viz $(\partial^2 V_\varphi^0/\partial T^2)_p$ indicate the structure maker properties of the solute [40][40]. This further supports that the charged end groups of amino acids are the predominant factors for the feature of temperature dependence of V_φ^0 of amino acids.

It is further seen from Table 2, that the values of transfer volumes, $V_{\varphi\,tr}^0$ are positive and increase monotonically with the molar concentration of xylose and temperature. The value of $V_{\varphi\,tr}^0$ is by definition free from solute-solute interaction and therefore provides information regarding solute solvent interactions [41]. The positive values of V_φ^0 and $V_{\varphi\,tr}^0$ for the l-histidine in aqueous xylose solutions could be explained by the co-sphere overlap model developed by Friedman and Krishnan [42]. The types of the interaction occurring between l-histidine and aqueous xylose can be classified as follows [43,44].

(a) The hydrophilic–ionic interaction between OH groups of xylose and zwitterions of l-histidine. (b) Hydrophilic–hydrophilic interaction the OH groups of xylose and NH groups in the side chain of acid l-histidine mediated through hydrogen bonding. (c) Hydrophilic–hydrophobic interaction between the OH groups of xylose molecule and non-polar ($-CH_2$) in the side chain of l-histidine molecule. (d) Hydrophobic–hydrophobic group interactions between the non-polar groups of xylose and non-polar ($-CH_2$) in the side chain of l-histidine molecule. Generally the values of $V_{\varphi\,tr}^0$ 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 $V_{\varphi\,tr}^0$ values in this work suggest that the hydrophilic–ionic group and hydrophilic– hydrophilic group interactions dominate in the studied systems [6, 7].

On viscometric property:

Furthermore, the solute-solvent interaction may be discussed through the change of dynamic property such as viscosity. From the table 1, it is seen that viscosity values increase with increase in concentration of solute (l-histidine).When a solute is dissolved in a solvent, some of the solvent molecules are attracted to the solute as the result of solute- solvent interaction and thus increase in solution viscosity. Generally the increase in viscosity of the solution on addition of solute indicates the structure making aspects of solutes [45].The viscosity B-coefficients provide information about the solvation of the solutes and their effects on the structure of the solvent in the near environment of the solute molecule. The viscosity B-coefficients(see table 2) originally introduced as an empirical term has been found to depend upon solute-solvent interactions and on the relative size of the solute and solvent molecules. The positive B-coefficient values obtained in the present systems indicate the strong solute-solvent interactions and also the structure making ability of the solute [46].

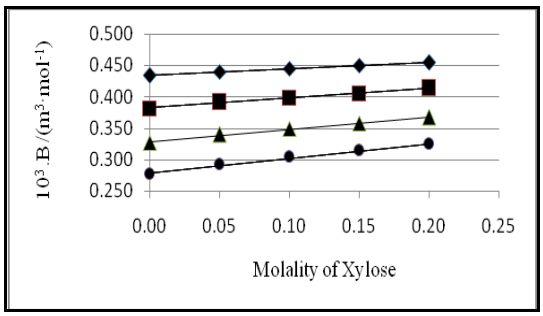

Figure 2. Variations of Jones-Dole coefficient, B vs. Molality of xylose, M_s, for l-histidine in xylose+ water solutions at temperatures, T/K=298.15, ♦; T/ K=303.15, ■; T/K=308.15, ▲; T/K=313.15, ●.

The *B* values decrease with increase in temperature (see figure 2), so their derivatives of temperature (dB/dT) are negative. The sign of (d*B*/d*T*) gives the information of structure making / breaking property of the solute in the solvent media[46] rather than simply the *B* coefficients. We see from Table 3 that (d*B*/d*T*) is negative for l-histidine showing the structure making ability of amino acids. Thus we can classify l-histidine is a structure maker in aqueous xylose solutions. The charged groups of amino acids in the present investigation

influence electrostatically the surrounding water resulting in the making of the solvent structure, through hydrophobic hydration. These are in excellent agreement with the conclusions drawn from $(\partial^2 V_\varphi^0/\partial T^2)_p$ discussed earlier.

It is of interest to add that the solvation of any solute can be judged from the magnitude of B/V_φ^0 .These values are listed in Table-2. A value between 0 and 2.5 indicates the unsolvated spherical species; and any higher value(>2.5) is an indication of solvated ones. In the present case, the values of B/V_φ^0 is > 2.5 substantiating the presence of solvated[47] spherical species in the reported systems .

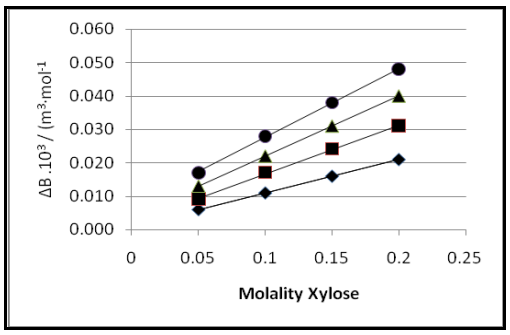

Figure 3. Variations of Jones-Dole coefficient, ΔB vs. Molality of xylose, M_s, for l-histidine in xylose+ water solutions at temperatures, T/K=298.15, ♦; T/ K=303.15, ■; T/K=308.15, ▲; T/K=313.15, ●.

From figure -3, it is clear that the value of ΔB_{tr} increases with concentration and temperature in all cases. Variation of ΔB_{tr} with concentration may be attributed to the dominance of hydrophilic–ionic interactions over the hydrophobic–ionic interactions[40].

Further, some activation parameters of viscous flow can also be obtained using B-Coefficients [48]. From Table 2, it is seen that the values of $\Delta\mu_2^{0*}$ are positive and larger than $\Delta\mu_1^{0*}$ indicating the structure making ability of the solute[28] thus supplementing our earlier findings through $(\partial^2 V_\varphi^0/\partial T^2)$ and (d*B*/d*T*) studies. Further, larger $\Delta\mu_2^{0*}$ values indicate the presence of stronger ion-solvent interactions. In other words the formation of the transition state is less favored in the presence of amino acids. This means that the formation of transition state is accompanied by the rapture and distortion of the intermolecular forces in solvent structure The positive $\Delta\mu_2^{0*}$ and $[\Delta G_2°(1\rightarrow 1')]$ values are larger than $\Delta\mu_1^{0*}$ values. Further both $\Delta\mu_2^{0*}$ and $[\Delta G_2° (1\rightarrow 1')]$ increase with the concentration of cosolute as well as temperature. This suggests that the formation of transition state is less favored in the presence of amino acids. This is due to the breaking and distortion of intermolecular bonds. This effectively means that more solute solvent bonds must be broken to form transition state. Similar reports are available in literature for α -amino acids in aqueous sodium acetate solution [30].

The pair interaction coefficients, V_{AB} / η_{AB} are positive while the triplet interaction coefficients, V_{ABB} / η_{ABB} are found to be negative and small(see table 4). The overall positive values of η_{AB} and V_{AB} indicate that interactions between the l- histidine in aqueous xylose solutions are mainly pair interactions. This also supports the conclusion drawn from the co-sphere overlap model that interactions occur due to the overlap of hydration spheres of the l-histidine and xylose

Conclusion:

The volumetric and viscometric results indicating the existence of strong solute–solvent (hydrophilic–ionic group and hydrophilic– hydrophilic group) interactions in the studied systems. Furthermore, the negative dB/dT values and the positive values of $(\partial^2 V_\varphi^0/\partial T^2)$ concludes the presence of structure making property of l-histidine in aqueous xylose solutions at all studied concentration and temperatures.

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