

Solute-Solute and Solute-Solvent Interactions of *l*-Methionine, *l*-Threonine and *l*-Histidine in Aqueous-Carbohydrate Solutions using Kirkwood-Buff Theory: A Theoretical Study



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Abstract

The Kirkwood-Buff (K-B) theory can be used to investigate the solute-solute, solute-solvent, solvent-solvent interactions in protein-aqueous carbohydrate system in terms of K-B integrals (G_{12} , G_{11} and G_{22}), which provide a direct estimation of these interactions. The K-B integrals nonpolar amino acid (*l*-methionine), positively charged polar amino acid (*l*-histidine) and neutral polar amino acid (*l*-threonine) in aqueous-glucose/sucrose (10% and 20% of glucose/sucrose in water, w/w) solvents have been evaluated from the ultrasonic speed and density data at 298.15 K. The results obtained by theoretical calculations are found in good agreement with those of experimental findings. It has been observed that there exist strong solute-solvent interactions in these systems.

Keywords: Kirkwood-Buff integrals; *l*-histidine; *l*-threonine; *l*-methionine; Solute-solvent interaction

Introduction

Proteins are the building blocks of body tissue and play important role in almost all the biological processes. But being too complex in nature their direct study is arduous. Since proteins are the polymer chains of amino acids linked together by peptide chains, therefore amino acids are studied as model constituents of proteins. The physicochemical and thermodynamic properties of amino acids in aqueous solutions provide valuable information on solute-solvent, solute-solute, and solvent-solvent interactions [1-4]. The stability of different conformations of protein is affected by different non-covalent interactions including electrostatic, hydrophobic interaction and hydrogen bonding. Therefore, to understand the stability factors of protein, it is important to study above mentioned interactions of amino acid in aqueous-saccharides system [5-8]. Carbohydrates are the polyhydroxy compounds which help in stabilizing globular structure of proteins [9,10]. The studies on carbohydrate-protein interactions are very important for the field of immunology, biosynthesis, pharmacology, and medicine. Because of conformational flexibility, saccharides play significant roles in many biological processes [11]. In living

organisms, interactions of saccharides with model molecules of proteins play a key role in understanding the thermodynamic behaviour of biochemical process in the body system [12,13].

Although a large amount of experimental data exists in the literature on the physicochemical properties of amino acids in aqueous and aqueous-carbohydrate solutions [14-21], but in contrast there are few reports on theoretical studies [22,23]. The Kirkwood and Buff [24] theory can be used for such kind of theoretical studies. K-B theory of solutions is a general statistical mechanical theory of solutions which is applicable to all types of intermolecular interactions and is valid both classically and quantum mechanically. This theory relates the radial distribution functions of various molecular species in a mixture to the derivatives of the thermodynamic properties of the species. It is one of the most accepted theories of solutions that directly correlate the thermodynamic quantities with the solution structure without any assumptions. In the present paper, K-B theory has been used to study solute-solvent, solute-solute and solvent-solvent interactions of *l*-methionine, *l*-threonine, and

l-histidine in aqueous-glucose/sucrose solvents (10% and 20% of glucose/sucrose in water, w/w). Density and ultrasonic speed data used in the present study have been taken from our previous studies [25-30].

Theory

The Kirkwood-Buff (KB) theory [24] expresses thermodynamic properties of a solution in terms of K-B integrals (G_{ij}). Mathematically it can be represented as

$$G_{ij} = \int_0^{\infty} (g_{ij}(r) - 1) 4\pi r^2 dr \quad (1)$$

where subscripts *i* and *j* refer to the two components that may be the same or different and g_{ij} is the pair correlation function, denoting the probability of finding a molecule of species *i* in a volume element at the distance *r* from the centre of a molecule of species *j*. The K-B integral G_{ij} represents the affinity of *i*th molecule towards *j*th molecule and vice-versa. This theory correlates compositional fluctuations to both integrals of the radial distribution functions of the different types of molecular pairs present in the solution as well as to the derivatives of the chemical potentials of different components.

Procedure to compute K-B integrals (G_{ij})

Subscripts 1 and 2 are used for solute (amino acid) and solvent (aqueous glucose/sucrose), respectively. KB integrals G_{12} , G_{11} , and G_{22} represent solute-solvent, solute-solute, and solvent-solvent interaction parameter respectively. Following equations were used to calculate these KB parameters [31,32]

$$G_{12} = G_{21} = RTK_T - (\bar{V}_1 \bar{V}_2 / DV) \quad (2)$$

where, *R* is the gas constant, *T* is the absolute temperature, *V* is the molar volume of the mixture, K_T is the isothermal compressibility, \bar{v}_2 is the partial molar volume of solvent (aqueous glucose/sucrose), \bar{v}_1 is the apparent molar volume of amino acid, *D* is the derivative of chemical potential. The \bar{v}_1 can be calculated using following relation

$$V_\phi = \frac{1000(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M}{\rho} \quad (3)$$

where *M* is the molar mass of the solute (amino acid), *m* is the molal concentration of the solute (amino acid), ρ and ρ_0 are the densities of the solution and the solvent, respectively. K_T can be calculated using following equation

$$K_T = K_S = \frac{1}{u^2 \rho} \quad (4)$$

where *u* is the ultrasonic speed in the solution. Here the K_T values of solvents are being used as the isothermal compressibility of solutions contributes negligibly to the G_{ij} values [33,34]. The parameter *D* in equation (2) is the derivative of chemical potential and can be solved using the equation

$$D = 1 + x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{P,T} \quad (5)$$

Here, x_1 and γ_1 are the mole fraction and activity coefficient of solute, respectively. The $\partial \ln \gamma_1 / \partial x_1$ term used in equation (4) can be obtained by plotting $\ln \gamma_1$ as a function mole fraction, x_1 of amino acid and taking the required slopes. The same could have been obtained by using the data of solvent activity coefficients and its mole fraction. Following equation was used to calculate the activity coefficients [35]

$$\ln \gamma_1 = x_2 w / kT \quad (6)$$

where *w* varies slightly with mole fraction and its value can be taken as 10^{-21} , *k* is the Boltzmann constant, x_2 is the mole fraction of solvent and *T* is the absolute temperature. Solute-solute and solvent-solvent interaction parameters, i.e., G_{11} and G_{22} can be calculated using solute-solvent interaction parameter G_{12}

$$G_{11} = G_{12} + (1/x_1) \left\{ (\bar{V}_2 / D) - V \right\} \quad (7)$$

$$G_{22} = G_{12} + (1/x_2) \left\{ (\bar{V}_1 / D) - V \right\} \quad (8)$$

Results and Discussion

The KB integrals for nonpolar amino acid (*l*-methionine), positively charged polar amino acid (*l*-histidine) and neutral polar amino acid (*l*-threonine) in aqueous-glucose/sucrose system were calculated using the above-mentioned procedure. The calculated values of K-B integrals along with experimental data used in calculation are listed in Tables 1-3. The variations of different K-B interaction parameters, i.e., G_{12} , G_{11} and G_{22} with x_1 (mole fraction of amino acid) for 10% and 20% concentration of glucose/sucrose in water (w/w) individually for *l*-methionine, *l*-threonine and *l*-histidine are shown graphically in Figures 1-6.

Figures 1&2 shows the variation of K-B integrals for *l*-methionine in aqueous-glucose/sucrose solution for different mole fractions of *l*-methionine. Figures 1a & 2a indicates that G_{12} the decrease with increase in *l*-methionine concentration in both aqueous-glucose and aqueous-sucrose systems. This suggests that solute-solvent interaction decrease with increase in *l*-methionine concentration, which in turn indicates the structure breaking ability of *l*-methionine in both these systems, which supported our earlier experimental studies [25,26] on these systems. In general, the types of interactions occurring between *l*-methionine and carbohydrate molecules can be classified as follows [36,37]

- The hydrophilic-ionic interaction between OH groups of carbohydrate molecules and zwitterions of *l*-methionine molecule.
- Hydrophilic-hydrophobic interaction between the OH groups of carbohydrate molecules and non-polar ($-CH_2$) inside chain of *l*-methionine molecule.
- Hydrophobic-hydrophobic group interactions between the non-polar groups of carbohydrate molecules and non-polar ($-CH_2$) inside chain of *l*-methionine molecule.

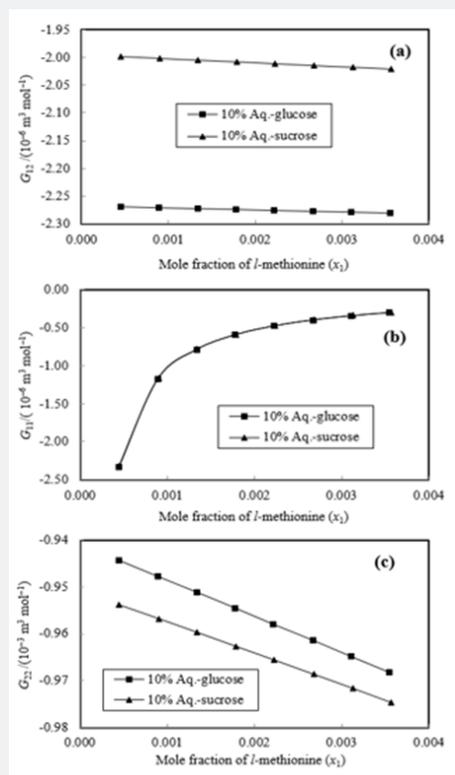


Figure 1: Plots of G_{12} , G_{11} and G_{22} against mole fraction (x_1) of *l*-methionine 10% glucose/sucrose + water at 298.15 K.

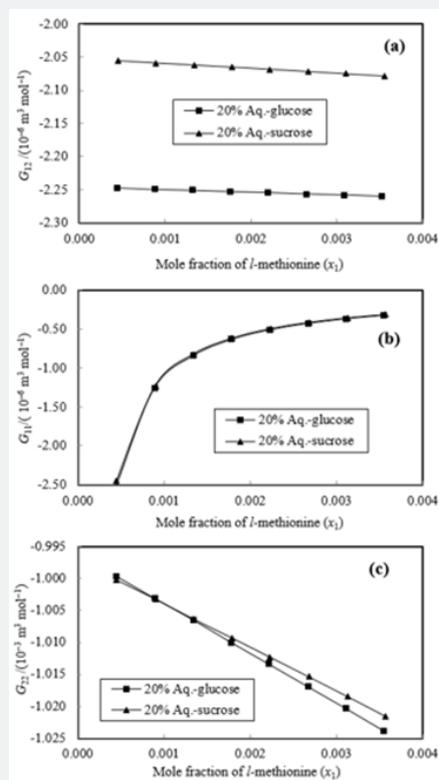


Figure 2: Plots of G_{12} , G_{11} and G_{22} against mole fraction (x_1) of *l*-methionine 20% glucose/sucrose + water at 298.15 K.

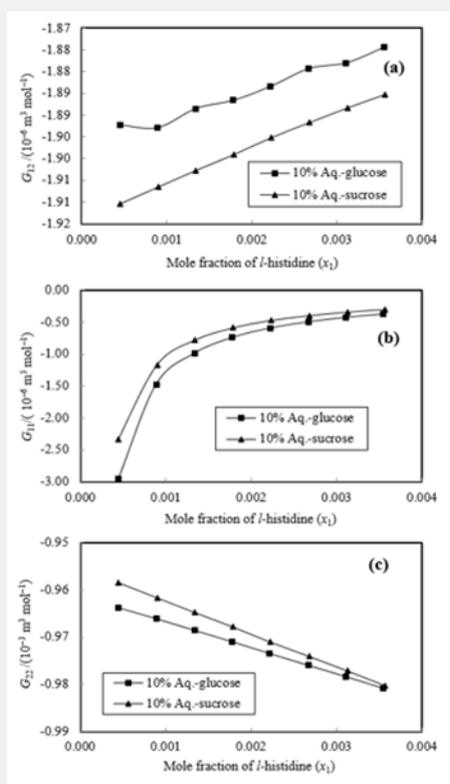


Figure 3: Plots of G_{12} , G_{11} and G_{22} against mole fraction (x_1) of I-histidine 10% glucose/sucrose + water at 298.15 K.

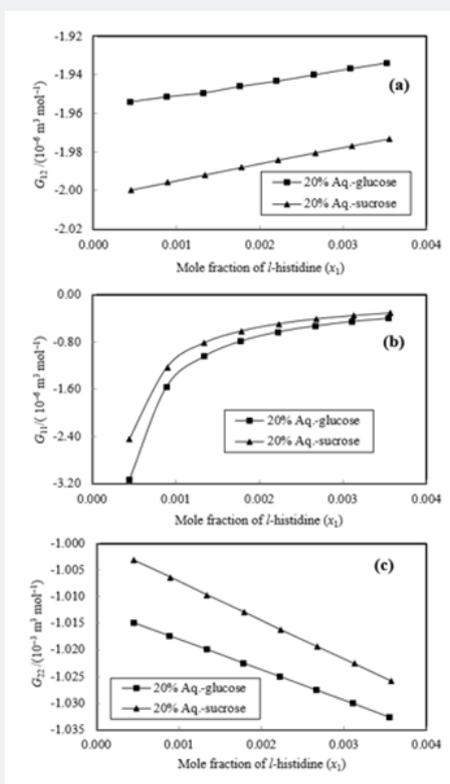


Figure 4: Plots of G_{12} , G_{11} and G_{22} against mole fraction (x_1) of I-histidine 20% glucose/sucrose + water at 298.15 K.

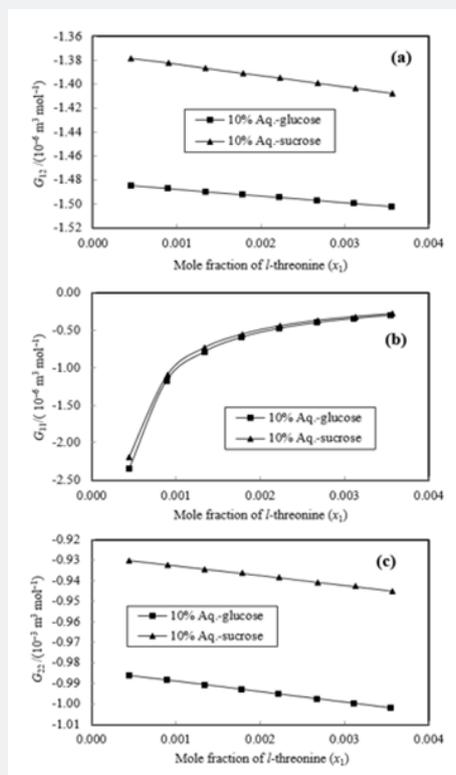


Figure 5: Plots of G_{12} , G_{11} and G_{22} against mole fraction (x_1) of l-threonine 10% glucose/sucrose + water at 298.15 K.

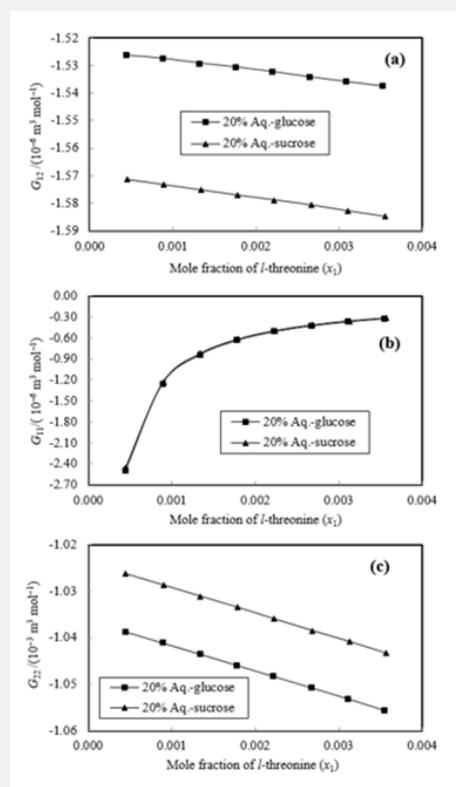


Figure 6: Plots of G_{12} , G_{11} and G_{22} against mole fraction (x_1) of l-threonine 20% glucose/sucrose + water at 298.15 K.

Table 1: Values of m , x_1 , ρ , u , V_ϕ , k_T , G_{12} , G_{11} and G_{22} for *l*-methionine in 10% and 20% glucose/sucrose + water solvents at 298.15 K.

m (mol kg ⁻¹)	x_1 (10 ⁻³)	ρ (kg m s ⁻¹)	u (m s ⁻¹)	$10^6 \cdot V_\phi$ (m ³ mol ⁻¹)	$10^{11} \cdot k_T$ (m ² N ⁻¹)	$10^6 \cdot G_{12}$ (m ³ mol ⁻¹)	$10^6 \cdot G_{11}$ (m ³ mol ⁻¹)	$10^3 \cdot G_{22}$ (m ³ mol ⁻¹)
<i>l</i>-Methionine in 10% aqueous-glucose								
0	0	1033.15	1530.6		4.132			
0.025	1.0336	1033.64	1531.5	126.15	4.125	-2.2696	-2.3526	-0.9443
0.05	1.0341	1034.11	1532.6	126.3	4.117	-2.2714	-1.1803	-0.9477
0.075	1.0346	1034.58	1533.9	126.42	4.108	-2.2729	-0.7895	-0.9511
0.1	1.035	1035.03	1535.3	126.55	4.099	-2.2745	-0.5943	-0.9545
0.125	1.0355	1035.48	1537	126.69	4.088	-2.2761	-0.4769	-0.958
0.15	1.0359	1035.91	1538.9	126.82	4.076	-2.2777	-0.3988	-0.9614
0.175	1.0363	1036.34	1540.9	126.95	4.064	-2.2793	-0.3429	-0.9649
0.2	1.0368	1036.76	1543.1	127.07	4.051	-2.2806	-0.3011	-0.9683
<i>l</i>-Methionine in 20% aqueous-glucose								
0	0	1070.31	1553.3		3.872			
0.025	1.0707	1070.66	1554.1	127.28	3.867	-2.2472	-2.5044	-0.9997
0.05	1.071	1070.99	1555	127.46	3.862	-2.2496	-1.2553	-1.0031
0.075	1.0713	1071.32	1556	127.58	3.855	-2.251	-0.8398	-1.0065
0.1	1.0716	1071.63	1557.3	127.73	3.848	-2.2529	-0.6317	-1.01
0.125	1.0719	1071.94	1558.7	127.87	3.84	-2.2546	-0.507	-1.0134
0.1499	1.0722	1072.23	1560.3	128.03	3.831	-2.2567	-0.4241	-1.0169
0.175	1.0725	1072.51	1562	128.17	3.822	-2.2584	-0.3645	-1.0203
0.1999	1.0728	1072.78	1563.9	128.33	3.811	-2.2604	-0.3201	-1.0238
<i>l</i>-Methionine in 10% aqueous-sucrose								
0	0	1037.45	1531.8		4.108			
0.025	1.0383	1038.32	1532.7	111.51	4.1	-1.9976	-2.3312	-0.9539
0.05	1.0392	1039.17	1533.9	111.73	4.09	-2.001	-1.1691	-0.9568
0.0749	1.04	1040	1535.2	111.97	4.08	-2.0045	-0.7828	-0.9597
0.1	1.0408	1040.82	1536.8	112.18	4.068	-2.0076	-0.5881	-0.9627
0.1249	1.0416	1041.61	1538.5	112.41	4.056	-2.0111	-0.4723	-0.9656
0.15	1.0424	1042.4	1540.5	112.65	4.042	-2.0147	-0.3945	-0.9686
0.175	1.0432	1043.16	1542.7	112.88	4.028	-2.018	-0.3391	-0.9716
0.2	1.0439	1043.91	1545	113.09	4.013	-2.0212	-0.2976	-0.9746
<i>l</i>-Methionine in 20% aqueous-sucrose								
0	0	1080.77	1555.3		3.825			
0.025	1.0814	1081.43	1556.2	115.35	3.818	-2.0557	-2.4541	-1.0002
0.05	1.0821	1082.08	1557.3	115.57	3.811	-2.059	-1.2307	-1.0032
0.075	1.0827	1082.7	1558.5	115.79	3.803	-2.0621	-0.8229	-1.0063
0.1	1.0833	1083.32	1559.8	116	3.794	-2.0651	-0.619	-1.0093
0.1249	1.0839	1083.91	1561.2	116.21	3.785	-2.0683	-0.4971	-1.0123
0.15	1.0845	1084.49	1562.8	116.44	3.775	-2.0716	-0.4151	-1.0154
0.175	1.0851	1085.05	1564.4	116.67	3.766	-2.075	-0.3569	-1.0185
0.1999	1.0856	1085.59	1566.2	116.89	3.755	-2.0783	-0.3134	-1.0216

Table 2: Values of m , x_1 , ρ , u , V_ϕ , k_T , G_{12} , G_{11} and G_{22} for l-histidine in 10% and 20% glucose/sucrose + water solvents at 298.15 K.

m (mol kg ⁻¹)	x_1 (10 ⁻³)	ρ (kg m s ⁻¹)	u (m s ⁻¹)	$10^6.V_\phi$ (m ³ mol ⁻¹)	$10^{11}.k_T$ (m ² N ⁻¹)	$10^6.G_{12}$ (m ³ mol ⁻¹)	$10^6.G_{11}$ (m ³ mol ⁻¹)	$10^3.G_{22}$ (m ³ mol ⁻¹)
<i>l</i>-Histidine in 10% aqueous-glucose								
0	0	1033.15	1530.6		4.132			
0.0199	1.0341	1034.1	1534.5	105.17	4.107	-1.8923	-2.9522	-0.9638
0.0399	1.0351	1035.06	1537.8	105.23	4.085	-1.8929	-1.4757	-0.9661
0.0599	1.036	1036.02	1540.6	105.02	4.067	-1.8885	-0.9852	-0.9686
0.0799	1.037	1036.98	1542.8	104.94	4.051	-1.8866	-0.7402	-0.971
0.1	1.0379	1037.94	1544.5	104.79	4.039	-1.8834	-0.5928	-0.9735
0.1199	1.0389	1038.91	1545.6	104.59	4.029	-1.8793	-0.4955	-0.976
0.14	1.0399	1039.87	1546.1	104.55	4.023	-1.878	-0.4253	-0.9784
0.16	1.0408	1040.84	1546.4	104.38	4.018	-1.8744	-0.3729	-0.9809
<i>l</i>-Histidine in 20% aqueous-glucose								
0	0	1070.31	1553.3		3.872			
0.0199	1.0711	1071.09	1556.9	110.67	3.852	-1.9541	-3.1405	-1.0149
0.0399	1.0719	1071.88	1560.2	110.54	3.833	-1.9514	-1.5698	-1.0174
0.0599	1.0727	1072.66	1563.2	110.46	3.815	-1.9494	-1.0479	-1.0199
0.0799	1.0735	1073.45	1565.8	110.29	3.8	-1.9459	-0.7873	-1.0225
0.1	1.0743	1074.25	1568.2	110.17	3.785	-1.9432	-0.6305	-1.025
0.1199	1.075	1075.04	1570.2	110.01	3.773	-1.9399	-0.527	-1.0276
0.14	1.0759	1075.85	1572	109.86	3.761	-1.9366	-0.4523	-1.0301
0.16	1.0767	1076.65	1573.3	109.71	3.752	-1.9336	-0.3966	-1.0327
<i>l</i>-Histidine in 10% aqueous-sucrose								
0	0	1037.45	1531.8		4.108			
0.0249	1.0386	1038.6	1535.6	106.64	4.083	-1.9105	-2.3402	-0.9585
0.0499	1.0398	1039.75	1538.9	106.46	4.061	-1.9066	-1.1711	-0.9617
0.0749	1.0409	1040.91	1541.8	106.28	4.041	-1.9028	-0.7824	-0.9648
0.0999	1.0421	1042.07	1544.1	106.12	4.025	-1.8991	-0.5883	-0.9679
0.125	1.0432	1043.24	1545.8	105.93	4.012	-1.8952	-0.4715	-0.9711
0.1499	1.0444	1044.4	1546.9	105.77	4.001	-1.8917	-0.3943	-0.9741
0.175	1.0456	1045.57	1547.5	105.62	3.994	-1.8883	-0.3387	-0.9772
0.1999	1.0467	1046.73	1547.5	105.48	3.989	-1.8852	-0.2973	-0.9803
<i>l</i>-Histidine in 20% aqueous-sucrose								
0	0	1080.77	1555.3		3.825			
0.025	1.0817	1081.68	1559.2	112.2	3.803	-1.9996	-2.4538	-1.0032
0.0499	1.0826	1082.6	1562.7	112.03	3.783	-1.9958	-1.2328	-1.0064
0.075	1.0835	1083.52	1565.8	111.84	3.764	-1.9918	-0.8226	-1.0097
0.0999	1.0845	1084.45	1568.6	111.66	3.748	-1.988	-0.6193	-1.0129
0.1249	1.0854	1085.38	1570.9	111.49	3.733	-1.9842	-0.4967	-1.0162
0.15	1.0863	1086.32	1573	111.32	3.72	-1.9805	-0.4147	-1.0194
0.1749	1.0873	1087.26	1574.6	111.15	3.71	-1.9769	-0.3567	-1.0226
0.2	1.0882	1088.2	1575.9	111	3.7	-1.9734	-0.3128	-1.0258

Table 3: Values of m , x_1 , ρ , u , V_ϕ , k_T , G_{12} , G_{11} and G_{22} for *l*-threonine in 10% and 20% glucose/sucrose + water solvents at 298.15 K.

m (mol kg ⁻¹)	x_1 (10 ⁻³)	ρ (kg m s ⁻¹)	u (m s ⁻¹)	$10^6 \cdot V_\phi$ (m ³ mol ⁻¹)	$10^{11} \cdot k_T$ (m ² N ⁻¹)	$10^6 \cdot G_{12}$ (m ³ mol ⁻¹)	$10^6 \cdot G_{11}$ (m ³ mol ⁻¹)	$10^3 \cdot G_{22}$ (m ³ mol ⁻¹)
<i>l</i>-Threonine in 10% aqueous-glucose								
0	0	1033.15	1530.6		4.132			
0.025	1.034	1034.02	1532.5	82.51	4.118	-1.4845	-2.3502	-0.9861
0.05	1.0349	1034.88	1534.5	82.69	4.104	-1.4871	-1.1778	-0.9883
0.075	1.0357	1035.73	1536.6	82.86	4.089	-1.4898	-0.787	-0.9906
0.0999	1.0366	1036.56	1538.9	83.03	4.074	-1.4922	-0.5922	-0.9929
0.1249	1.0374	1037.39	1541.1	83.18	4.059	-1.4945	-0.4748	-0.9952
0.15	1.0382	1038.2	1543.5	83.35	4.043	-1.497	-0.3963	-0.9975
0.175	1.039	1039	1546.1	83.53	4.026	-1.4997	-0.3405	-0.9998
0.2	1.0398	1039.78	1548.8	83.69	4.009	-1.5021	-0.2986	-1.0021
<i>l</i>-Threonine in 20% aqueous-glucose								
0	0	1070.31	1553.3		3.872			
0.025	1.071	1071.02	1555.5	86.45	3.859	-1.5263	-2.5	-1.0387
0.05	1.0717	1071.72	1557.9	86.55	3.845	-1.5275	-1.2528	-1.0411
0.075	1.0724	1072.41	1560.3	86.67	3.83	-1.5292	-0.8371	-1.0435
0.0999	1.0731	1073.09	1562.7	86.78	3.816	-1.5306	-0.6299	-1.0459
0.1249	1.0738	1073.76	1565.4	86.9	3.801	-1.5323	-0.505	-1.0483
0.15	1.0744	1074.42	1568.1	87.04	3.785	-1.5342	-0.4214	-1.0507
0.175	1.0751	1075.07	1571.1	87.16	3.768	-1.5359	-0.3621	-1.0531
0.2	1.0757	1075.71	1574.4	87.29	3.75	-1.5375	-0.3175	-1.0556
<i>l</i>-Threonine in 10% aqueous-sucrose								
0	0	997.07	1496.9		4.476			
0.025	0.9981	998.14	1501.1	76.54	4.446	-1.3784	-2.192	-0.9301
0.05	0.9992	999.18	1505.5	76.78	4.416	-1.3822	-1.0986	-0.9322
0.075	1.0002	1000.22	1510.2	77.05	4.384	-1.3866	-0.7341	-0.9343
0.0999	1.0012	1001.23	1515.2	77.31	4.35	-1.3909	-0.5525	-0.9364
0.1249	1.0022	1002.23	1520.5	77.55	4.316	-1.3947	-0.4429	-0.9385
0.15	1.0032	1003.21	1526.1	77.82	4.28	-1.399	-0.3697	-0.9407
0.175	1.0042	1004.18	1531.9	78.07	4.244	-1.4032	-0.3177	-0.9428
0.2	1.0051	1005.12	1538.1	78.34	4.205	-1.4075	-0.2786	-0.945
<i>l</i>-Threonine in 20% aqueous-sucrose								
0	0	1080.77	1555.3		3.825			
0.025	1.0814	1081.41	1559.5	88.18	3.802	-1.5715	-2.4526	-1.0263
0.05	1.082	1082.04	1563.9	88.32	3.779	-1.5734	-1.2292	-1.0287
0.075	1.0827	1082.66	1568.6	88.45	3.754	-1.5753	-0.8214	-1.0311
0.0999	1.0833	1083.27	1573.6	88.59	3.728	-1.5772	-0.6181	-1.0335
0.1249	1.0839	1083.87	1578.9	88.71	3.701	-1.5789	-0.4955	-1.036
0.15	1.0845	1084.46	1584.5	88.85	3.673	-1.5808	-0.4136	-1.0385
0.175	1.085	1085.04	1590.3	89	3.644	-1.5829	-0.3553	-1.0409
0.2	1.0856	1085.6	1596.5	89.14	3.614	-1.5849	-0.3117	-1.0434

The magnitude of solute-solvent interaction in aqueous-sucrose is larger than that of aqueous-glucose for same concentration of *l*-methionine. This can be explained based on greater hydrophilic-ionic group interactions in sucrose molecules due to presence of more hydroxyl groups as compared to glucose molecules. Figures 1b & 2b shows the variation of G_{11} representing solute-solute interaction of *l*-methionine in aqueous-glucose/sucrose media. It has almost same magnitude in both glucose and sucrose media with sudden increase for 0.0005 mole fraction to 0.015 mole fraction of *l*-methionine then gradual increase for rest of the compositions till 0.0040 mole fraction. Solvent-solvent interactions, G_{22} show linear decrease with increase in *l*-methionine concentration (Figures 1c & 2c) in aqueous-glucose/sucrose indicating that the solvent-solvent interaction decreases with increase in *l*-methionine concentration, which further reflects that the solute-solvent interaction dominates in these systems.

The K-B integrals of *l*-histidine in aqueous-glucose/sucrose system are shown in Figures 3 & 4. Figures 3a & 4a indicate that G_{12} the increase with increase in *l*-histidine concentration in both aqueous-glucose and aqueous-sucrose systems. This suggests that solute-solvent interaction increase with increase in *l*-histidine concentration, indicating the structure making ability of *l*-histidine in both these systems, which supported our earlier experimental studies [37,28] on these systems. The interactions occurring between *l*-histidine and carbohydrate molecules can be classified as follows [38,39]

- i. The hydrophilic-ionic interaction between OH groups of carbohydrate molecules and zwitterions of *l*-histidine molecule.
- ii. Hydrophilic-hydrophilic interaction between the OH groups of carbohydrate molecules and NH groups in the side chain of *l*-histidine mediated through hydrogen bonding.
- iii. Hydrophilic-hydrophobic interaction between the OH groups of carbohydrate molecules and non-polar ($-\text{CH}_2$) inside chain of *l*-histidine molecule.
- iv. Hydrophobic-hydrophobic group interactions between the non-polar groups of carbohydrate molecules and non-polar ($-\text{CH}_2$) inside chain of *l*-histidine molecule.

The variation of K-B parameter G_{11} representing solute-solute interaction among *l*-histidine molecules in aqueous-glucose/sucrose media are shown in Figures 3b & 4b. Almost similar trend and magnitude was observed for *l*-histidine in both the media with sudden increase initially and almost constant value for higher *l*-histidine concentration. Figures 3c & 4c represents solvent-solvent interaction parameter, G_{22} , which decrease continuously with *l*-histidine concentration indicating that the solvent-solvent interaction decreases with increase in *l*-histidine concentration, which further reflects that the solute-solvent interaction dominates over solute-solute and solvent-solvent interactions in these systems.

The K-B integrals of *l*-threonine in aqueous-glucose/sucrose solvents are shown in Figures 5 & 6. Figures 5a & 6a indicate

that G_{12} the decrease with increase in *l*-threonine concentration in both aqueous-glucose and aqueous-sucrose systems. This suggests that solute-solvent interaction decrease with increase in *l*-threonine concentration, indicating the structure breaking ability of *l*-threonine in both these systems, which supported our earlier conclusions derived from experimental volumetric, ultrasonic, and viscometrical properties [29,30] of these systems. The interactions occurring between *l*-threonine and carbohydrate molecules following types of interactions are possible [38,39]

- a) The hydrophilic-ionic interaction between OH groups of carbohydrate molecules and zwitterions of *l*-threonine.
- b) Hydrophilic-hydrophilic interaction the OH groups of carbohydrate molecules and OH groups in the side chain of acid *l*-threonine mediated through hydrogen bonding.
- c) Hydrophilic-hydrophobic interaction between the OH groups of carbohydrate molecules molecule and non-polar ($-\text{CH}_2$) inside chain of *l*-threonine molecule.
- d) Hydrophobic-hydrophobic group interactions between the non-polar groups of carbohydrate molecules and non-polar ($-\text{CH}_2$) inside chain of *l*-threonine molecule.

Figures 5b & 6b variation of K-B parameter G_{11} representing solute-solute interaction among *l*-threonine molecules in aqueous-glucose/sucrose solvents, wherein sudden increase followed by very small increase in interaction with increase in *l*-threonine concentration is visible. The magnitude of all the three interaction parameters (G_{12} , G_{11} and G_{22}) is negative, but as compared to G_{12} and G_{11} has higher negative values. This confirms weaker solute-solute interaction and comparatively stronger solute-solvent interaction. A perusal of Figures 5c & 6c reveals that the solvent-solvent interaction parameter, G_{22} decreases continuously with increase in *l*-threonine concentration indicating that the solvent-solvent interaction decreases with increase in *l*-threonine concentration, which further reveals that the solute-solvent interaction dominates over solute-solute and solvent-solvent interactions in these systems.

Conclusion

The K-B integrals of nonpolar amino acid (*l*-methionine) positively charged polar amino acid (*l*-histidine) and neutral polar amino acid (*l*-threonine) in aqueous-glucose/sucrose (10% and 20% of glucose/sucrose in water, w/w) solvents have been evaluated from the ultrasonic speed and density data at 298.15K using the Kirkwood-Buff theory. The results indicated that solute-solvent interactions (hydrophilic-ionic interaction) between OH groups of carbohydrate molecules and zwitterions of these amino acid dominates over solute-solute and solvent-solvent interactions in these systems, and solute-solvent is found to increase with carbohydrate concentration. The variation of G_{12} with amino acid concentration revealed that *l*-histidine acts as structure maker while *l*-methionine and *l*-threonine act as structure breaker in these systems.

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