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Effect of concentration and temperature variations on interactions in (L-serine/L-valine + aqueous glucose/sucrose/lactose) systems: Viscometric and activation parametric study

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Viscosities of (L-serine/L-valine + 0.1 mol dm^{-3} aqueous glucose/sucrose/lactose) systems have been measured as a function of molal concentration of amino acids at different temperatures; 293.15 K, 298.15 K, 303.15 K, 308.15 K and 313.15 K. The viscosity data has been utilized to determine viscosity *B*-coefficients employing Jones-Dole equation. The viscosity *B*-coefficients of transfer ($\Delta_{tr}B$), variation of *B* with temperature (*dB/dT*) and solvation number (S_n) of L-serine/L-valine have been obtained using the experimental viscosity values. Further, Gibbs free energy of activation of viscous flow per mole of solvent ($\Delta\mu^{\circ\#}_1$) as well as per mole of solute ($\Delta\mu^{\circ\#}_2$) along with activation enthalpy ($\Delta H^{\circ\#}_2$) and entropy ($\Delta S^{\circ\#}_2$) have been computed using Feakin's transition state theory to throw light on the mechanism of viscous flow. The results have been discussed in terms of solute-solvent interactions; and structure making tendency of amino acid molecules in aqueous saccharides solutions.

Keywords: Viscosity, Amino acids, Saccharides, Viscosity B-coefficients, Activation parameters

1 Introduction

Amino acid, as a basic unit of protein has been in use for studies on the solvation and conformation of proteins which in turn provides valuable information on molecular interactions[1-4]. The polyhydroxy compounds, for example saccharides, are widely distributed in various forms of life as essential moieties and play significant role in many biological processes[5-7]. They also play a key role in stabilizing the native conformations of proteins/enzymes. The stabilization of native conformations of proteins has been related to various non-covalent interactions like hydrogen bonding, electrostatic, hydrophobic, etc.[8-12]. The study of these interactions provides important insight into the conformational stability and folding/unfolding of globular proteins[13-15]. Saccharides are very essential for energy metabolism in organisms and configuration of biological molecules. Saccharides have grasped more attention for their ability to protect biological macromolecules. Saccharides are important chemicals in life processes because of their conformational flexibility, saccharides play significant role in bimolecular recognition[16,17]. The complex conformational and configurational factors determining the structure of proteins in sugar solution makes the study of protein-sugar interactions difficult and interesting. One of the useful approaches involves studying the model components of proteins, i.e., amino acids in aqueous and mixed aqueous saccharides solutions.

Jones-Dole or viscosity B-coefficients values is considered to be a vital parameter to describe the structure maker or structure breaker nature of solute in various solvents. By means of the researches on the transport properties of amino acids in the solutions of aqueous saccharides, one can gather useful information about the solute-solute and solute-solvent interactions, which turns to be helpful in understanding the mechanism of protein stabilization through saccharides[2,18,19]. Glucose is a simple sugar with the molecular formula $C_6H_{12}O_6$. Glucose circulates in the blood of animals as blood sugar. It is made during photosynthesis from water and carbon dioxide, using energy from sunlight. It is the most important source of energy for cellular respiration. Glucose is stored as a polymer, in plants as starch and in animals as glycogen. It is used as an energy source in most organisms, from bacteria to humans, either through aerobic respiration, anaerobic respiration, or fermentation. Sucrose is the organic compound

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commonly known as table sugar and sometimes called saccharose. In sucrose, the components glucose and fructose are linked through an ether bond between glucosyl subunit and the fructosyl unit[20]. The bond is called a glycosidic linkage. Lactose is a disaccharide derived from the condensation of galactose and glucose, which forms a β-1→4 glycosidic linkage. Infant mammals nurse on their mothers to drink milk, which is rich in lactose. The intestinal villi secrete the enzyme called lactase (β-D-galactosidase) to digest it. This enzyme cleaves the lactose molecule into its two subunits, the simple sugars glucose and galactose, which can be absorbed. Since lactose occurs mostly in milk, in most mammals, the production of lactase gradually decreases with maturity due to a lack of continuing consumption.

Literature survey shows a comprehensive study on transport properties of amino acids[21-26], however, viscometric work of the interactions between amino acids in aqueous solutions of different saccharides and their comparative behaviour seem to be scarce. One of the reasons of studying viscometric properties in conjunction with volumetric properties is that many amino acids and their derivatives are known as compensatory or compatible solutes in stabilizing proteins and enhancing enzyme activity[27-29]. So, this prompted us to evaluate the transport behaviour of L-serine and L-valine with three saccharides (glucose, sucrose and lactose) in aqueous medium. Hence, in continuation to our previous work[30,31], we are reporting the nature of these two amino acids in aqueous saccharides depending upon viscosity *B*-coefficients, viscosity *B*-coefficients of transfer, solvation number, Gibbs free energy and other related thermodynamic activation parameters of viscous flow from T = 293.15 K to 313.15 K and 1 atmospheric pressure.

2 Experimental

2.1 Source and purity of chemicals

The specifications of the chemicals used in the present work are L-serine, L-valine and α-lactose monohydrate (all >99.8%), D-(+)-glucose and sucrose (both >99.5%). All these chemicals are obtained from Sigma Aldrich, India and used after storing them over anhydrous calcium chloride in a vacuum desiccator overnight at room temperature, except α-lactose monohydrate which was used as such. Freshly prepared triple distilled water was used for preparing solutions of amino acids and saccharides.

2.2 Apparatus and procedure

The solutions were prepared on molality basis using an electronic single pan five digit analytical balance (Model: Mettler AE-240) with a precision of ±0.01 mg. The aqueous solutions of glucose, sucrose and lactose (each being 0.1 mol dm^{-3}) were used as solvent to prepare L-serine and L-valine solutions of nine different molal concentrations (ranging from 0.025 to 0.2) mol kg^{-1}. The solutions were prepared with utmost care and stored in special airtight bottles to avoid their exposure to air and evaporation. The viscosity of the solutions was measured by using an Ubbelohde viscometer, calibrated at 298.15 K with distilled water and pure methanol. In order to avoid the thermal fluctuation of solutions in viscometer, the solution was immersed for about half an hour in a thermostatic water bath. The time of flow was noticed using an electronic watch with the resolution of 0.01 s. An Average of at least five sets reproducible within ±0.1 s was used with sufficient care. The accuracy in measurements of viscosity was within $\pm 1\times10^{-6}$ N s m^{-2}. An electronic controlled thermostatic water bath (Model: TIC-4000N, Thermotech, India) was used to maintain the temperature of the solutions to an accuracy of ±0.02 K.

3 Results and Discussion

3.1 Viscometric studies

The experimental values of viscosity of different molalities of amino acids (L-serine and L-valine) in pure water and aqueous solutions of saccharides (0.1 glucose, 0.1 sucrose and 0.1 lactose) mol dm^{-3} as a function temperature (Table 1) are calculated using the density data already reported in the literature[41]. It is evident that viscosity continually increases with increasing molal concentration of L-serine/L-valine and decreases with increasing temperature in all the investigated systems. A representative 3-D plot of viscosity, η, versus molality, m, of L-serine/L-valine in aqueous 0.1 mol dm^{-3} lactose solution is displayed in Fig. 1. With an increase in temperature, there is typically an increase in the molecular interchange as molecules move faster at higher temperature. In liquid state, there will be molecular interchange similar to those developed in a gas, but there are additional substantial attractive, cohesive forces between the molecules of a liquid (which are much closer together than those of a gas). Both cohesion and molecular interchange factors contribute to liquid viscosity. The impact of increasing the temperature of a liquid is to

Table 1 — Viscosity (η) and reduced viscosity $\{(\eta_r\text{-}1)/m^{1/2}\}$ of solutions of L-serine and L-valine of different molalities in water and aqueous saccharides at different temperatures.

m (mol kg^{-1})	T (K) 293.15		298.15		303.15		308.15		313.15	
	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)
L-serine + water										
0.000	1.0019		0.8903		0.7973		0.7190		0.6526	
0.025	1.0092	0.0460	0.8961	0.0409	0.8023	0.0397	0.7238	0.0423	0.6562	0.0347
0.050	1.0165	0.0651	0.9013	0.0555	0.8067	0.0527	0.7275	0.0531	0.6598	0.0491
0.075	1.0234	0.0783	0.9070	0.0686	0.8112	0.0639	0.7316	0.0639	0.6631	0.0588
0.100	1.0300	0.0888	0.9125	0.0787	0.8160	0.0740	0.7356	0.0728	0.6663	0.0663
0.125	1.0373	0.1000	0.9178	0.0873	0.8210	0.0842	0.7398	0.0817	0.6695	0.0731
0.150	1.0434	0.1070	0.9237	0.0968	0.8256	0.0916	0.7437	0.0888	0.6726	0.0793
0.175	1.0503	0.1155	0.9295	0.1051	0.8302	0.0985	0.7480	0.0965	0.6758	0.0850
0.200	1.0572	0.1235	0.9351	0.1125	0.8349	0.1056	0.7519	0.1023	0.6793	0.0916
L-serine + 0.1 mol dm^{-3} aqueous-glucose										
0.000	1.1705		0.9613		0.8295		0.7637		0.7629	
0.025	1.1825	0.0649	0.9703	0.0595	0.8368	0.0559	0.7696	0.0485	0.7686	0.0477
0.050	1.1944	0.0912	0.9793	0.0838	0.8442	0.0795	0.7764	0.0746	0.7745	0.0679
0.075	1.2063	0.1118	0.9884	0.1031	0.8517	0.0979	0.7828	0.0912	0.7803	0.0834
0.100	1.2186	0.1300	0.9973	0.1183	0.8589	0.1122	0.7891	0.1053	0.7858	0.0951
0.125	1.2306	0.1452	1.0067	0.1337	0.8667	0.1268	0.7950	0.1160	0.7919	0.1076
0.150	1.2420	0.1578	1.0160	0.1468	0.8744	0.1396	0.8014	0.1273	0.7975	0.1172
0.175	1.2534	0.1694	1.0254	0.1593	0.8815	0.1498	0.8080	0.1385	0.8041	0.1292
0.200	1.2653	0.1811	1.0345	0.1702	0.8890	0.1605	0.8144	0.1485	0.8102	0.1388
L-serine + 0.1 mol dm^{-3} aqueous-sucrose										
0.000	1.1088		0.9907		0.8873		0.7939		0.7054	
0.025	1.1239	0.0863	1.0013	0.0675	0.8962	0.0637	0.8022	0.0662	0.7129	0.0673
0.050	1.1381	0.1181	1.0127	0.0991	0.9058	0.0933	0.8101	0.0911	0.7198	0.0916
0.075	1.1522	0.1430	1.0248	0.1258	0.9162	0.1187	0.8182	0.1116	0.7262	0.1077
0.100	1.1656	0.1619	1.0358	0.1441	0.9257	0.1367	0.8263	0.1289	0.7334	0.1255
0.125	1.1810	0.1842	1.0473	0.1615	0.9353	0.1531	0.8347	0.1454	0.7401	0.1392
0.150	1.1949	0.2005	1.0591	0.1784	0.9452	0.1686	0.8431	0.1601	0.7476	0.1543
0.175	1.2097	0.2175	1.0708	0.1933	0.9549	0.1822	0.8516	0.1737	0.7544	0.1659
0.200	1.2239	0.2322	1.0824	0.2070	0.9642	0.1937	0.8603	0.1871	0.7614	0.1776
L-serine + 0.1 mol dm^{-3} aqueous-lactose										
0.000	1.1243		0.9768		0.8676		0.7923		0.7496	
0.025	1.1397	0.0866	0.9889	0.0786	0.8775	0.0723	0.8011	0.0701	0.7581	0.0707
0.050	1.1550	0.1222	1.0013	0.1123	0.8877	0.1035	0.8097	0.0983	0.7655	0.0941
0.075	1.1700	0.1483	1.0135	0.1372	0.8982	0.1290	0.8186	0.1212	0.7731	0.1141
0.100	1.1864	0.1747	1.0251	0.1562	0.9088	0.1503	0.8276	0.1411	0.7810	0.1318
0.125	1.2002	0.1909	1.0376	0.1762	0.9183	0.1654	0.8357	0.1549	0.7885	0.1465
0.150	1.2152	0.2087	1.0498	0.1929	0.9285	0.1813	0.8447	0.1709	0.7968	0.1622
0.175	1.2306	0.2260	1.0625	0.2096	0.9385	0.1954	0.8533	0.1839	0.8034	0.1712
0.200	1.2448	0.2397	1.0752	0.2252	0.9488	0.2093	0.8620	0.1968	0.8122	0.1863
L-valine + water										
0.000	1.0019		0.8903		0.7973		0.7190		0.6526	
0.025	1.0092	0.0458	0.8968	0.0464	0.8025	0.0411	0.7231	0.0361	0.6557	0.0303

(contd.)

Table 1 — Viscosity (η) and reduced viscosity $\{(\eta_r\text{-}1)/m^{1/2}\}$ of solutions of L-serine and L-valine of different molalities in water and aqueous saccharides at different temperatures. *(contd.)*

m (mol kg^{-1})	T (K) 293.15		298.15		303.15		308.15		313.15	
	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)
0.050	1.0163	0.0644	0.9028	0.0628	0.8073	0.0560	0.7274	0.0525	0.6589	0.0434
0.075	1.0236	0.0790	0.9089	0.0762	0.8122	0.0684	0.7318	0.0649	0.6623	0.0543
0.100	1.0313	0.0929	0.9146	0.0864	0.8173	0.0792	0.7359	0.0742	0.6658	0.0638
0.125	1.0382	0.1024	0.9211	0.0977	0.8221	0.0881	0.7396	0.0810	0.6691	0.0716
0.150	1.0450	0.1112	0.9267	0.1057	0.8270	0.0962	0.7436	0.0884	0.6723	0.0778
0.175	1.0520	0.1196	0.9336	0.1162	0.8324	0.1053	0.7480	0.0965	0.6751	0.0825
0.200	1.0587	0.1268	0.9386	0.1214	0.8369	0.1111	0.7517	0.1016	0.6785	0.0888
L-valine + 0.1 mol dm^{-3} aqueous-glucose										
0.000	1.1705		0.9613		0.8295		0.7637		0.7629	
0.025	1.1823	0.0639	0.9707	0.0618	0.8380	0.0648	0.7702	0.0541	0.7680	0.0421
0.050	1.1936	0.0882	0.9802	0.0878	0.8459	0.0883	0.7769	0.0774	0.7734	0.0614
0.075	1.2061	0.1109	0.9890	0.1053	0.8538	0.1071	0.7841	0.0978	0.7794	0.0788
0.100	1.2179	0.1281	0.9991	0.1242	0.8614	0.1217	0.7901	0.1092	0.7848	0.0907
0.125	1.2294	0.1423	1.0085	0.1388	0.8689	0.1345	0.7966	0.1218	0.7908	0.1036
0.150	1.2409	0.1553	1.0175	0.1509	0.8765	0.1464	0.8035	0.1347	0.7965	0.1137
0.175	1.2537	0.1699	1.0265	0.1621	0.8847	0.1591	0.8094	0.1432	0.8014	0.1207
0.200	1.2651	0.1807	1.0357	0.1730	0.8927	0.1704	0.8150	0.1501	0.8071	0.1295
L-valine + 0.1 mol dm^{-3} aqueous-sucrose										
0.000	1.1088		0.9907		0.8873		0.7939		0.7054	
0.025	1.1225	0.0782	1.0019	0.0717	0.8965	0.0653	0.8022	0.0665	0.7119	0.0585
0.050	1.1362	0.1107	1.0137	0.1040	0.9057	0.0927	0.8110	0.0963	0.7185	0.0828
0.075	1.1496	0.1345	1.0260	0.1301	0.9150	0.1140	0.8195	0.1178	0.7253	0.1031
0.100	1.1635	0.1561	1.0380	0.1509	0.9258	0.1372	0.8276	0.1344	0.7319	0.1186
0.125	1.1769	0.1738	1.0495	0.1678	0.9348	0.1515	0.8354	0.1480	0.7384	0.1323
0.150	1.1917	0.1930	1.0608	0.1827	0.9445	0.1665	0.8438	0.1623	0.7446	0.1435
0.175	1.2062	0.2099	1.0724	0.1971	0.9543	0.1804	0.8523	0.1757	0.7511	0.1547
0.200	1.2208	0.2258	1.0839	0.2103	0.9640	0.1932	0.8599	0.1859	0.7577	0.1657
L-valine + 0.1 mol dm^{-3} aqueous-lactose										
0.000	1.1243		0.9768		0.8676		0.7923		0.7497	
0.025	1.1387	0.0810	0.9887	0.0773	0.8778	0.0740	0.8004	0.0648	0.7569	0.0609
0.050	1.1535	0.1162	1.0006	0.1090	0.8874	0.1019	0.8094	0.0965	0.7640	0.0852
0.075	1.1688	0.1444	1.0125	0.1334	0.8974	0.1256	0.8185	0.1205	0.7714	0.1059
0.100	1.1840	0.1679	1.0256	0.1581	0.9078	0.1464	0.8265	0.1365	0.7778	0.1184
0.125	1.1984	0.1864	1.0370	0.1742	0.9180	0.1643	0.8348	0.1517	0.7853	0.1344
0.150	1.2135	0.2049	1.0492	0.1915	0.9283	0.1805	0.8431	0.1657	0.7927	0.1482
0.175	1.2268	0.2180	1.0611	0.2064	0.9391	0.1969	0.8512	0.1777	0.7998	0.1597
0.200	1.2411	0.2325	1.0732	0.2206	0.9486	0.2088	0.8593	0.1890	0.8073	0.1719

reduce the cohesive forces while simultaneously increasing the rate of molecular interchange. The former effect causes a decrease in the shear stress while the latter causes it to increase. Thus, the lowering of viscosity as a result of impact of increasing temperature may be due to the accelerated molecular motion in the system.

The relative viscosity, η_r, which is related to the molality, m, may be expressed using Jones-Dole equation[32]:

$$\eta_r = \frac{\eta}{\eta_o} = 1 + Am^{1/2} + Bm \qquad \cdots (1)$$

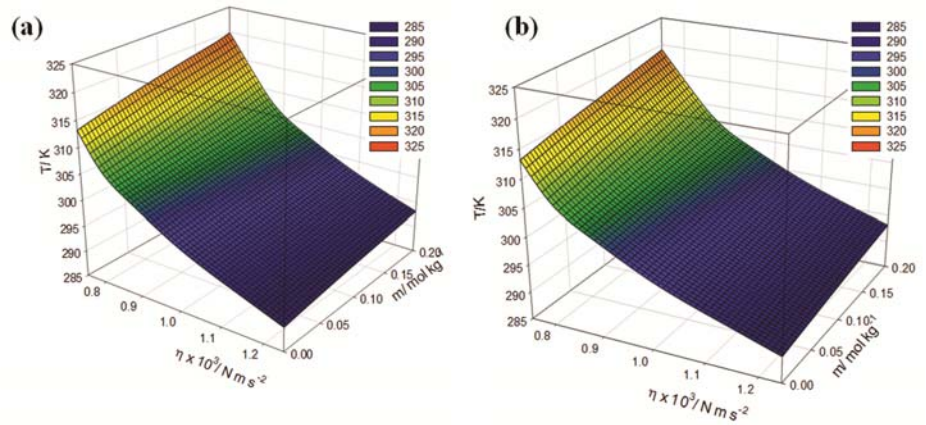

Fig. 1 — Variation of viscosity (η) with molality (m) for (a) L-serine, and (b) L-valine in 0.1 mol dm^{-3} aqueous lactose at 293.15 K, 298.15 K, 303.15 K, 308.15 K and 313.15 K.

where η_o and η are viscosities of solvent (aqueous saccharide) and solution (amino acid + water + saccharide), respectively. A called as Falkenhagen coefficient, is a constant which arises from ion-ion or solute–solute interactions. B, called also as viscosity B-coefficients or Jones-Dole coefficient, which measures the size, shape, charge and structural effects is regarded as an important parameter to study solute-solvent interactions[33-35]. The A-coefficients (values not given) for L-serine and L-valine is found to be much smaller in magnitude as compared to B-coefficients and, hence, can be considered negligible in case of non-electrolytes[36].

The values of reduced viscosity, $(\eta_r\text{-}1)/m^{1/2}$, of solutions of different molalities of L-serine and L-valine in water and aqueous saccharides are presented in Table 1 and plotted in Figs. 2 (A) and (B), respectively. Accordingly, viscosity B-coefficients, found to be linear at all concentrations and temperatures, are estimated using a plot between reduced viscosity and square root of molality by least squares analysis method. An analysis of Table 2 reveals that the values of viscosity B-coefficients for L-serine in water show a reasonable agreement with literature value[33]. The positive B-coefficients for both the amino acids at all temperatures show the dominance of solute-solvent interactions over solute-solute interactions. As is evident from Table 2, B-coefficients of amino acids in aqueous saccharides are larger than in water indicating that in presence of co-solute (saccharide), the structure of solution gets strengthened. The values of B-coefficients increase with the increase in the complexity of saccharide solutions in the order: glucose < sucrose < lactose. An increase in B-coefficients values from glucose to lactose (Fig. 3) may be attributed to the formation of structure that allows the solute to act on solvent and reinforce its structure by hydrogen bonding[37]. Thus, the inference drawn from B-coefficients supports the behaviour of an existence of strong solute-solvent interactions which further advocates the existence of strong ionic-hydrophillic and hydrophilic-hydrophillic interactions.

From Table 2 it is also evident that B-coefficients show a decreasing trend with rise in temperature. The information regarding structure-making or structure-breaking capability of the solute is well documented by considering the temperature derivative of B-coefficients, dB/dT[32]. The negative values of dB/dT (Table 2) suggest that nature of both L-serine and L-valine is that of structure-maker in aqueous saccharides. The structure-making ability of L-serine in aqueous d-xylose/l-arabinose and L-valine in aqueous sorbital solutions has also been observed by Nain *et al.*[33] and Ren *et al.*[38], respectively.

The viscosity B-coefficients of transfer, $\Delta_{tr}B$, of L-serine and L-valine from water to aqueous glucose/sucrose/lactose solutions has been evaluated using the relation:

$$\Delta_{tr}B = B_{aq\text{-}saccharides} - B_{water} \quad \ldots (2)$$

where B_{water} is B-coefficients of L-serine/L-valine in water. The $\Delta_{tr}B$ values reported in Table 2 follow the order: L-valine < L-serine, which indicates a more structured medium in case of L-serine than L-valine. Further, for a particular amino acid, increase in $\Delta_{tr}B$ values in the order of glucose < sucrose < lactose (Fig. 4) may be due to greater dehydration effect of

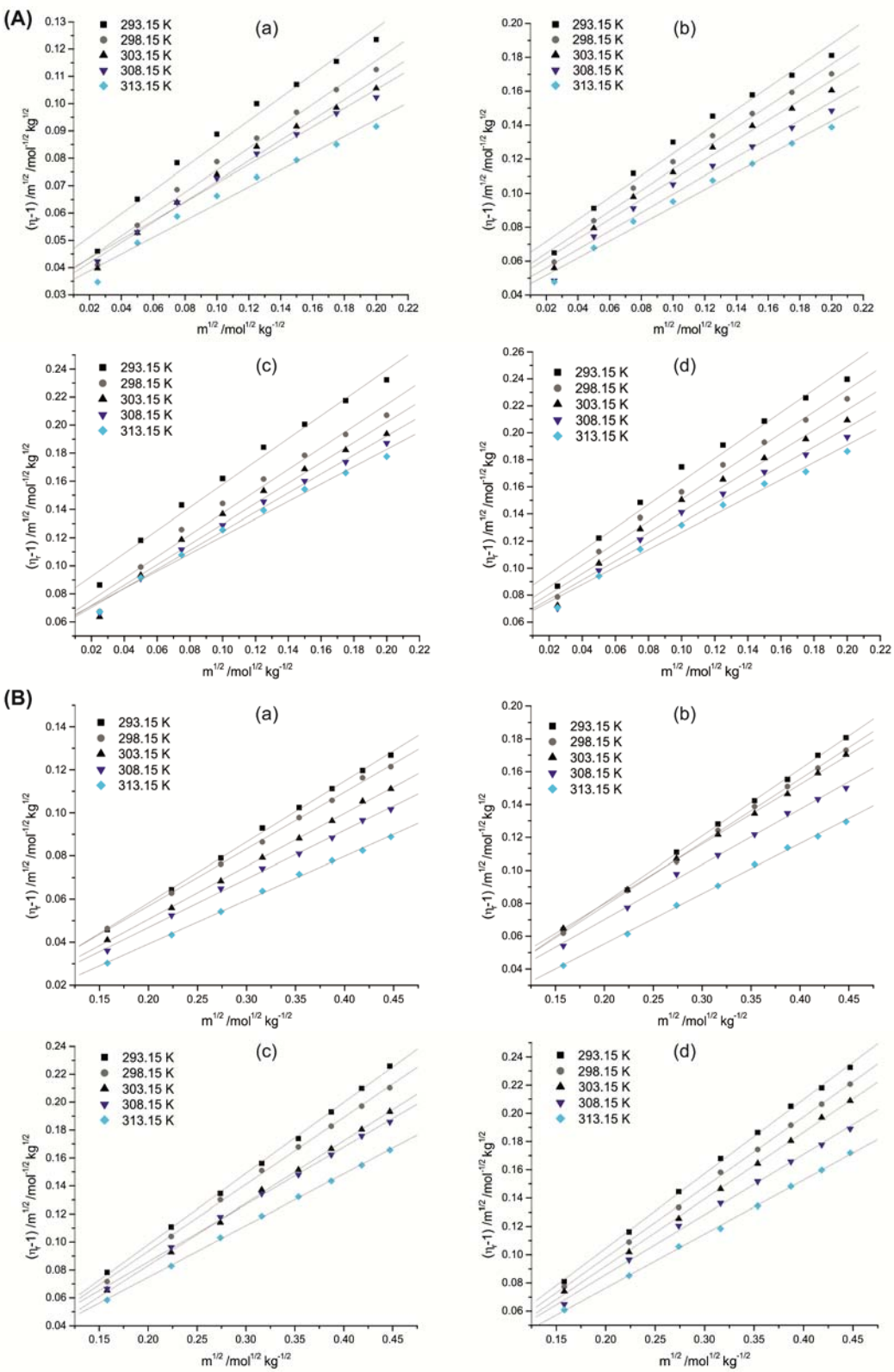

Fig. 2 — (A) Variation of reduced viscosity $\{(\eta_r\text{-}1)/m^{1/2}\}$ with molality ($m^{1/2}$) of L-serine in (a) water, (b) 0.1 mol dm^{-3} glucose, (c) 0.1 mol dm^{-3} sucrose, (d) 0.1 mol dm^{-3} lactose, at different temperatures and (B) Variation of reduced viscosity $\{(\eta_r\text{-}1)/m^{1/2}\}$ with molality ($m^{1/2}$) of L-valine in (a) water, (b) 0.1 mol dm^{-3} glucose, (c) 0.1 mol dm^{-3} sucrose, (d) 0.1 mol dm^{-3} lactose, at different temperatures.

Table 2 — Viscosity *B*-coefficients and viscosity *B*-coefficients of transfer ($\Delta_{tr}B$) of L-serine and L-valine in aqueous saccharides at different temperatures and temperature coefficient (*dB/dT*).

System	T (K) 293.15	298.15	303.15	308.15	313.15	*dB/dT* ($dm^3mol^{-1}K^{-1}$)
	Viscosity *B*-coefficients (dm^3mol^{-1})/ Viscosity *B*-coefficients of transfer (dm^3mol^{-1})					
L-serine + water	0.265(±0.003)	0.249(±0.003)	0.231(±0.004)	0.212(±0.005)	0.192(±0.003)	-0.004(±0.001)
L-serine + 0.1 mol dm^{-3} aqueous glucose	0.403(±0.003)/ 0.138	0.384(±0.002)/ 0.135	0.362(±0.002)/ 0.131	0.338(±0.005)/ 0.126	0.313(±0.004)/ 0.121	-0.005(±0.001)
L-serine + 0.1 mol dm^{-3} aqueous sucrose	0.506(±0.006)/ 0.241	0.481(±0.004)/ 0.232	0.452(±0.004)/ 0.221	0.419(±0.005)/ 0.207	0.383(±0.006) / 0.191	-0.006(±0.001)
L-serine + 0.1 mol dm^{-3} aqueous lactose	0.531(±0.006)/ 0.266	0.503(±0.004)/ 0.254	0.472(±0.005)/ 0.241	0.438(±0.003)/ 0.226	0.400(±0.006)/ 0.208	-0.007(±0.001)
L-valine + water	0.282(±0.004)	0.264(±0.004)	0.245(±0.002)	0.225(±0.004)	0.203(±0.003)	-0.004 ±0.001)
L-valine + 0.1 mol dm^{-3} aqueous glucose	0.407(±0.004)/ 0.125	0.386(±0.004)/ 0.122	0.362(±0.003)/ 0.117	0.335(±0.008)/ 0.110	0.305(±0.005)/ 0.102	-0.005(±0.001)
L-valine + 0.1 mol dm^{-3} aqueous sucrose	0.509(±0.006) 0.227	0.479(±0.005)/ 0.215	0.446(±0.005)/ 0.201	0.410(±0.005)/ 0.185	0.370(±0.003)/ 0.167	-0.007(±0.001)
L-valine + 0.1 mol dm^{-3} aqueous lactose	0.526(±0.007)/ 0.244	0.498(±0.004)/ 0.234	0.473(±0.005)/ 0.228	0.425(±0.008)/ 0.200	0.382(±0.005)/ 0.179	-0.007(±0.001)

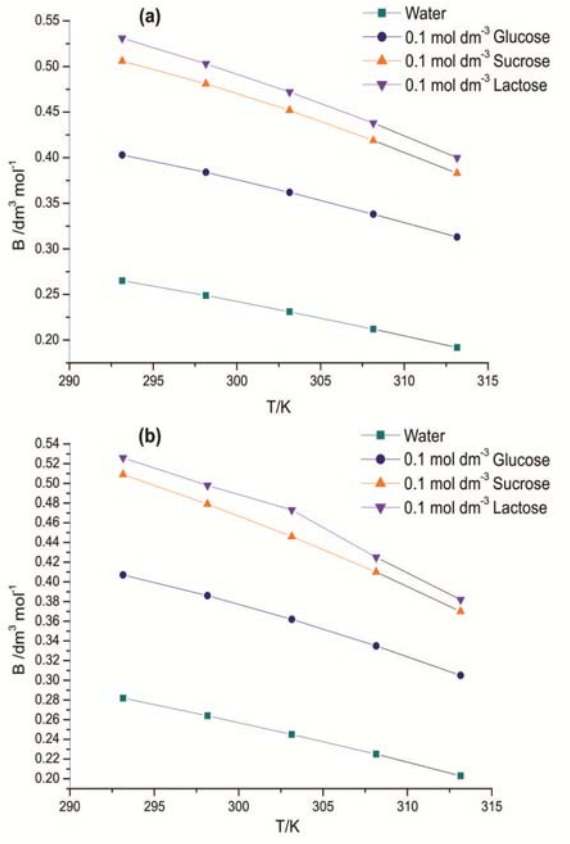

Fig. 3 — Variation of Jones-Dole coefficient (*B*) with temperature (*T*) for (a) L-serine, and (b) L-valine in water and aqueous saccharides.

lactose than sucrose which is again greater than glucose, i.e., the higher $\Delta_{tr}B$ value is due to interactions of solute in solvent which cause the release of electrostrictive water molecules into the bulk water. Glucose molecule is a monosaccharide, whereas both sucrose and lactose has two monosaccharide units with the difference that the lactose molecule has galactose and glucose subunits whereas the sucrose molecule consists of glucose and fructose subunits. The lactose and sucrose has equal number of OH groups but the former consisting of galactose and glucose subunits has the most moderate and disturbed hydration layers[39] than sucrose molecule which consists of glucose and fructose subunits. Therefore, lactose molecule does not fit well into the structure of water, or one can say that it has poor compatibility with the three-dimensional hydrogen-bonded structure of water. Hence, it interacts strongly with L-serine/L-valine and resulting dehydration contributes more positive values to $\Delta_{tr}B$ than sucrose molecule. In other words, the main contribution to *B*-coefficients of transfer values comes from the interactions between charged centres of amino acids and saccharides molecules, rather than from interactions between R groups of amino acids and saccharides molecules. The above trend is due to strong ionic-hydrophilic and hydrophilic-hydrophilic interactions of L-serine/L-valine in aqueous lactose and sucrose solutions than in glucose one. $\Delta_{tr}B$ values show a decreasing trend with increasing temperature for the current system. Similar results are reported by Banipal *et al.*[40].

3.2 Solvation number

The solvation number (S_n, Table 3) is calculated from the ratio of *B*-coefficients to apparent molar volume

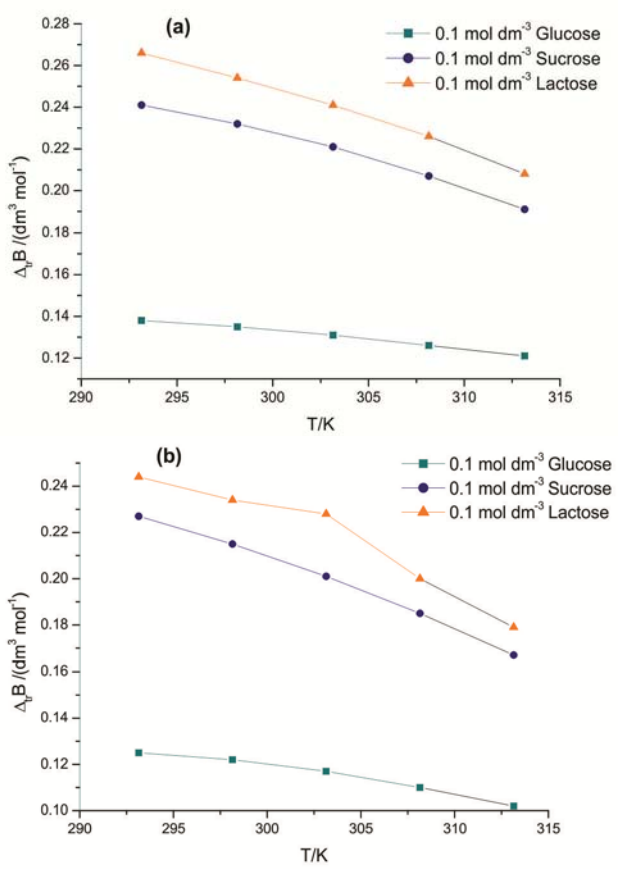

Fig. 4 — Variation of B-coefficients of transfer ($\Delta_t B$) with temperature (T) for (a) L-serine, and (b) L- valine in water and aqueous saccharides.

($B/V°_\phi$) at infinite dilution (for $V°_\phi$ values: see Table 3[41]). These values are an important indicator for solvated and unsolvated spherical solute species. For an unsolvated spherical species, the value of S_n lies between 0 and 2.5[2,42] whilst a value greater than 2.5 is an indicator of solvated spherical solute molecules. In this work, S_n values for L-serine and L-valine in aqueous saccharides are greater relative to water stating that solvation of solutes gets increased in presence of co-solutes (saccharides). The solvation effect of saccharides increase in the order of: glucose < sucrose < lactose. The values of solvation number in both the amino acids decrease with increase in temperature which may be attributed to the competition among various interactions prevailing in the system.

3.3 Thermodynamics of viscous flow

According to the transition state theory[43], each and every solvent molecule per mole of the solution, bonded less or more strongly with solute, must be accompanied by a transition. This model can be used to evaluate the thermodynamic parameters from the viscosities of L-serine/L-valine in aqueous saccharides. The Gibbs free energy of activation or chemical potential per mole of solvent, $\Delta\mu^{\circ\#}_1$, is obtained from the following relation.

$$\eta_o = \left(\frac{hN_A}{V^\circ_1}\right) exp\left(\frac{\Delta\mu^{\circ\#}_1}{RT}\right) \quad \cdots (3)$$

which upon rearrangement gives:

$$\Delta\mu^{\circ\#}_1 = RT\, ln\left(\frac{\eta_o V^\circ_1}{hN_A}\right) \quad \cdots (4)$$

where N_A, h, R and T are Avogadro's number, Planck's constant, universal gas constant and temperature, respectively. $V^\circ_1 (= \Sigma x_i M_i / \rho_o)$ is the mean apparent molar volume of mixed solvents (glucose/sucrose/lactose + water). x_i and M_i are the mole fraction and molar weight of water and aqueous-saccharides solutions and ρ_o is the density of the solvent. Based upon the transition state theory, it has been postulated by Feakins *et al.*[44,45] that the activation Gibbs energy is related to viscosity B-coefficients using the following expression:

$$B = \frac{(V^\circ_1 - V^\circ_2) + V^\circ_1(\Delta\mu^{\circ\#}_2 - \Delta\mu^{\circ\#}_1)/RT}{1000} \quad \cdots (5)$$

Rearrangement of above equation gives activation Gibbs free energy for viscous flow per mole of the solute, $\Delta\mu^{\circ\#}_2$,:

$$\Delta\mu^{\circ\#}_2 = \Delta\mu^{\circ\#}_1 + \left(\frac{RT}{V^\circ_1}\right)[1000B - (V^\circ_1 - V^\circ_2)] \quad \cdots (6)$$

Here, $V^\circ_2 (= V^\circ_\phi)$ is the limiting apparent molar volume of the solute. The calculated values of $\Delta\mu^{\circ\#}_1$, V°_1 and $\Delta\mu^{\circ\#}_2$ at various temperatures are summarized in Table 4. The values of $\Delta\mu^{\circ\#}_2$ signify the capability to form the transition state via the solute-solvent interactions from the ground state of the solvent. The values of $\Delta\mu^{\circ\#}_2$ are large and positive than those of $\Delta\mu^{\circ\#}_1$ for amino acids in aqueous and aqueous-saccharides reflecting that interactions between L-serine/L-valine and aqueous saccharides in the ground state are stronger than in the transition state. In other words, the formation of a transition state is less favoured in presence of L-serine/L-valine which also means that the formation of the transition state is accompanied by the rupture and distortion of intermolecular forces in aqueous saccharides. Feakins

et al.[46] has reported that those solutes which have large values of $\Delta\mu^{\circ}_{2}{}^{\#}$ are structural makers. The large value of $\Delta\mu^{\circ}_{2}{}^{\#}$ obtained in the study confirms this view point, which supports the result as discussed earlier. However, decrease in $\Delta\mu^{\circ}_{2}{}^{\#}$ values with increase in temperature (Fig. 5) shows that low temperature is more suited for the formation of transition state. Hence, the increase in solute-solvent interactions becomes apparent when the system is subjected to increase in temperature. It has also been observed that $\Delta\mu^{\circ}_{2}{}^{\#}$ values increase as complexity of saccharides increases from glucose to lactose, which is due to the strengthening of L-serine/L-valine-saccharide interactions. The similar results were observed by Kumar *et al*.[37] and Riyazuddeen and Usmani[47].

The activation entropy, $\Delta S^{\circ}_{2}{}^{\#}$, and activation enthalpy, $\Delta H^{\circ}_{2}{}^{\#}$ values for the viscous flow of L-serine and L-valine in water and aqueous-saccharides solutions are obtained using the following equations:

$$\Delta S^{\circ}_{2}{}^{\#} = -\left(\frac{d\Delta\mu^{\circ}_{2}{}^{\#}}{dT}\right) \quad \cdots(7)$$

$$\Delta H^{\circ}_{2}{}^{\#} = \Delta\mu^{\circ}_{2}{}^{\#} + T\Delta S^{\circ}_{2}{}^{\#} \quad \ldots(8)$$

The values reported in Table 4 shows that for both amino acids values of $\Delta H^{\circ}_{2}{}^{\#}$ and $T\Delta S^{\circ}_{2}{}^{\#}$ are positive which indicates that the formation of the transition state is associated with bond breaking and the decrease in order of the system[37]. Thus, $\Delta H^{\circ}_{2}{}^{\#}$ and

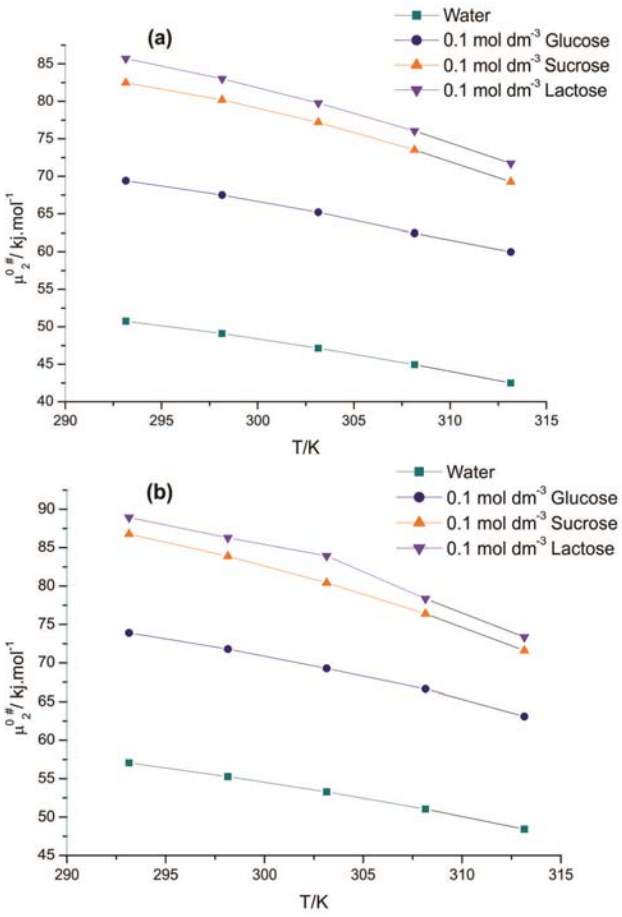

Fig. 5 — Variation of Gibbs free energy of activation per mole of solute ($\Delta\mu^{\circ}_{2}{}^{\#}$) with temperature ($T$) for (a) L-serine, and (b) L-valine in water and aqueous saccharides.

Table 3 — Limiting apparent molar volume (V°_{ϕ}) and solvation number (S_n) values for L-serine and L-valine in water and aqueous saccharides at different temperatures.

System	T (K)				
	293.15	298.15	303.15	308.15	313.15
			B/V°_{ϕ}		
L-serine + water	4.42	4.13	3.81	3.49	3.14
L-serine + 0.1 mol dm^{-3} aqueous glucose	6.55	6.21	5.83	5.43	5.02
L-serine + 0.1 mol dm^{-3} aqueous sucrose	8.04	7.62	7.14	6.61	6.02
L-serine + 0.1 mol dm^{-3} aqueous lactose	8.42	7.95	7.45	6.90	6.29
L-valine + water	3.14	2.93	2.71	2.47	2.23
L-valine + 0.1 mol dm^{-3} aqueous glucose	4.47	4.22	3.94	3.64	3.30
L-valine + 0.1 mol dm^{-3} aqueous sucrose	5.51	5.17	4.80	4.41	3.97
L-valine + 0.1 mol dm^{-3} aqueous lactose	5.69	5.37	5.09	4.57	4.10

Table 4 — Apparent (partial) molar volume of solvent (V°_1), Gibbs free energy of activation for solvent ($\Delta\mu^{\circ\#}_1$), Gibbs free energy of activation for solute, ($\Delta\mu^{\circ\#}_2$), $T\Delta S^{\circ\#}_2$, activation enthalpy ($\Delta H^{\circ\#}_2$) for L-serine and L-valine in water and aqueous saccharides at different temperatures.

T(K)	$V^{o}_1 \times 10^6$ (m^3mol^{-1})	$\Delta\mu^{\circ\#}_1$ ($kJmol^{-1}$)	$\Delta\mu^{\circ\#}_2$ ($kJmol^{-1}$)	$T\Delta S^{\circ\#}_2$ ($kJmol^{-1}$)	$\Delta H^{\circ\#}_2$ ($kJmol^{-1}$)
		L-serine + water			
293.15	18.05	9.30	50.74	-120.95	-70.21
298.15	18.07	9.16	49.11	-123.02	-73.91
303.15	18.09	9.04	47.15	-125.08	-77.93
308.15	18.12	8.93	44.94	-127.14	-82.20
313.15	18.16	8.83	42.51	-129.21	-86.70
		L-serine + 0.1 mol dm^{-3} aqueous glucose			
293.15	18.22	9.70	69.41	-140.13	-70.72
298.15	18.24	9.38	76.72	-142.52	-75.02
303.15	18.26	9.17	65.19	-144.91	-79.72
308.15	18.29	8.96	62.46	-147.69	-84.84
313.15	18.33	9.26	59.98	-149.69	-89.71
		L-serine + 0.1 mol dm^{-3} aqueous sucrose			
293.15	18.41	9.59	82.47	-194.00	-111.53
298.15	18.43	9.48	80.19	-197.32	-117.13
303.15	18.46	9.36	77.20	-200.62	-123.42
308.15	18.49	9.24	73.52	-203.93	-130.41
313.15	18.52	9.08	69.26	-207.24	-137.98
		L-serine + 0.1 mol dm^{-3} aqueous lactose			
293.15	18.44	9.63	85.71	-204.85	-119.14
298.15	18.46	9.45	83.01	-208.35	-125.34
303.15	18.49	9.31	79.77	-211.84	-132.07
308.15	18.52	9.24	76.05	-215.34	-139.29
313.15	18.55	9.25	71.72	-218.83	-147.11
		L-valine + water			
293.15	18.05	9.30	57.06	-126.23	-69.17
298.15	18.07	9.16	55.27	-128.38	-73.11
303.15	18.09	9.04	53.28	-130.54	-77.26
308.15	18.12	8.93	51.04	-132.69	-81.65
313.15	18.16	8.83	48.41	-134.84	-86.43
		L-valine +0.1 mol dm^{-3} aqueous glucose			
293.15	18.22	9.70	73.90	-157.07	-83.17
298.15	18.24	9.38	71.79	-159.75	-87.96
303.15	18.26	9.17	69.29	-162.43	-93.14
308.15	18.29	8.96	66.62	-165.11	-98.49
313.15	18.33	9.26	63.09	-167.79	-104.70
		L-valine + 0.1 mol dm^{-3} aqueous sucrose			
293.15	18.41	9.59	86.77	-221.86	-135.09
298.15	18.43	9.48	83.89	-225.64	-141.75
303.15	18.46	9.36	80.42	-229.42	-149.00
308.15	18.49	9.24	76.39	-233.21	-156.82
313.15	18.52	9.08	71.60	-236.99	-165.39
		L-valine + 0.1 mol dm^{-3} aqueous lactose			
293.15	18.44	9.63	88.93	-229.24	-140.31
298.15	18.46	9.45	86.29	-233.15	-146.86
303.15	18.49	9.31	83.93	-237.06	-153.13
308.15	18.52	9.24	78.35	-240.97	-162.62
313.15	18.55	9.25	73.35	-244.88	-171.53

$T\Delta S^{\circ}_{2}{}^{\#}$ values support the conclusions drawn from the earlier discussion of $\Delta\mu^{\circ}_{2}{}^{\#}$ values. $\Delta H^{\circ}_{2}{}^{\#}$ and $T\Delta S^{\circ}_{2}{}^{\#}$ values has been found to increase with increase in the complexity of saccharides showing that the formation of activated species for viscous flow becomes difficult in the ternary systems.

4 Conclusions

The viscosities of solutions of two amino acids (L-serine and L-valine) in water and in aqueous (0.1 glucose, 0.1 sucrose and 0.1 lactose) mol dm^{-3} are measured at different temperatures. From the experimental results, viscosity *B*-coefficients, its temperature derivative, transfer parameter, solvation and various activation parameters are evaluated. The obtained values of *B*-coefficients and its transfer counterpart are positive which signifies that amino acid-saccharide-water interactions are stronger than amino acid-amino acid interactions. The negative values of *dB/dT* have been argued for the structure-making behaviour of these amino acids in aqueous-saccharides solutions. The values of $\Delta\mu^{\circ}_{2}{}^{\#}$ reveal that the formation of transition state is less favoured in terms of energy for the current systems and hence validating the effective structure maker behaviour of amino acids in solutions of aqueous-saccharides. Moreover, the accomplishment of the transition state is associated by bond breaking and decrease in order as validated by positive $\Delta H^{\circ}_{2}{}^{\#}$ and $T\Delta S^{\circ}_{2}{}^{\#}$ values.

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