

## Apparent molar volumes and viscosities of solutions of mono- and disaccharides in water and in (DMSO + water) mixed solvent systems at 293.15, 303.15 and 313.15 K

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**Abstract :** Apparent molar volumes ( $V_\phi$ ) and viscosities ( $\eta$ ) of solutions of mono- and disaccharides viz. glucose, fructose, sucrose and maltose have been determined in water and in dimethyl sulphoxide (DMSO) + water solvent systems of varying composition (10, 20 and 30%, w/w) at 293.15, 303.15 and 313.15 K as a function of molal concentration of saccharides. The  $V_\phi$  and  $\eta$  data have been analysed in the light of equations,  $V_\phi = V_\phi^0 + S_\nu m$  and  $(\eta_{rel} - 1)/\sqrt{m} = A + B\sqrt{m}$  respectively. The activation thermodynamic quantities ( $\Delta\mu_2^{0\#}$ ,  $\Delta H_2^{0\#}$  and  $\Delta S_2^{0\#}$ ) of viscous flow for mono- and disaccharides in water and in (DMSO + water) mixed solvent systems have been determined at 293.15, 303.15 and 313.15 K. The results in regard to solute-solvent and solute-solute interactions in water and in (DMSO + water) mixed solvent systems have been discussed in terms of the values of  $V_\phi^0$ ,  $S_\nu$  and those of  $A$  and  $B$ . The values of limiting apparent molar expansibilities ( $\phi_E^0$ ) and that of  $(\partial^2 V_\phi^0 / \partial T^2)_p$  have been determined from temperature dependence of  $V_\phi^0$ . The results of the study reveal that mono- and disaccharides behave as structure-makers in water and also in (DMSO + water) mixed solvent systems of varying composition.

**Keywords :** Apparent molar volumes, viscosities, mono- and disaccharides, mixed solvents.

### Introduction

In continuation of our earlier publications<sup>1,2</sup> relating to the studies of apparent molar volumes and viscosities of solutions of mono- and disaccharides in mixed solvent systems of (acetonitrile + water) and (formamide + water) at different temperatures, we now report the results of our studies for the solutions of mono- and disaccharides in water and in dimethyl sulphoxide (DMSO) + water mixed solvent systems of varying composition at different temperatures with a view to ascertain the nature of solute-solute and solute-solvent interactions in the light of the following aspects : (i) Determination of apparent molar volume ( $V_\phi$ ) from density as a function of molal concentration ( $m$ ) of solutions of glucose, fructose, sucrose and maltose in water and also in (DMSO + water) mixed solvent systems of varying composition (10, 20 and 30%, w/w) at 293.15, 303.15 and 313.15 K; (ii) Determination of limiting apparent molar volume ( $V_\phi^0$ ) of glucose, fructose, sucrose and maltose in water as well as in (DMSO + water) mixed solvent systems at different

temperatures; (iii) Determination of partial molar volumes of transfer ( $V_{2,ir}^0$ ) of glucose, fructose, sucrose and maltose from water to (DMSO + water) mixed solvent systems at different temperatures; (iv) Determination of viscosities of solutions of glucose, fructose, sucrose and maltose in water and in (DMSO + water) mixed solvent systems at different temperatures, and subsequent analysis of viscosity-concentration ( $m$ ) data in the light of Jones-Dole equation; (v) Determination of the values of limiting apparent molar expansibilities ( $\phi_E^0$ ) and that of  $(\partial^2 V_\phi^0 / \partial T^2)_p$  from temperature dependence of  $V_\phi$ ; and (vi) Determination of free energies of activation of viscous flow,  $\Delta\mu_1^{0\#}$  and  $\Delta\mu_2^{0\#}$  per mole of solvent and solute respectively, at different temperatures and subsequent calculation of entropy ( $\Delta S_2^{0\#}$ ) and enthalpy ( $\Delta H_2^{0\#}$ ) of activation of viscous flow at different temperatures.

### Results and discussion

*Variation of apparent molar volume ( $V_\phi$ ) of mono- and disaccharides with molality ( $m$ ) in (DMSO + water)*

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*mixed solvent systems of varying composition at different temperatures :*

The apparent molar volumes ( $V_\phi$ ) of mono- and disaccharides viz. glucose, fructose, sucrose and maltose in water as well as in (DMSO + water) mixed solvent systems have been determined as a function of molality ( $m$ ) from the density data at 293.15, 303.15 and 313.15 K using the following equation<sup>3,4</sup>,

$$V_\phi = \frac{1000(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M}{\rho} \quad (1)$$

where  $m$  is the molality of the solutions,  $M$  is the molecular weight of the solute (mono- and disaccharides);  $\rho_0$  and  $\rho$  are the densities of solvent and solution respectively. The representative data in respect of glucose in

0% and 10% (DMSO + water) mixed systems are presented in Table 1. The plots of  $V_\phi$  versus  $m$  are found to be linear in water as well as in mixed solvent systems of (DMSO + water) at different temperatures. These are presented in representative Figs. 1 and 2. The variation of  $V_\phi$  with  $m$  can therefore be represented by the following equation<sup>3,4</sup>,

$$V_\phi = V_\phi^0 + S_v m \quad (2)$$

where  $V_\phi^0$  is the limiting apparent molar volume at infinite dilution (which is equal to the partial molar volume of the solute,  $V_2^0$ ) and  $S_v$  is the experimental slope<sup>5</sup> (sometimes considered to be the volumetric pairwise interaction coefficient<sup>6,7</sup>).  $V_\phi^0$  is a measure of solute-solvent interactions<sup>8</sup> while  $S_v$  is a measure of solute-solute interactions<sup>9</sup>. The parameters,  $V_\phi^0$  and  $S_v$  have been evaluated

**Table 1.** Densities ( $\rho$ ) and apparent molar volumes ( $V_\phi$ ) of mono- and disaccharides as a function of molality ( $m$ ) in (DMSO + water) mixed solvent systems at different temperatures

Saccharides	Molality ( $m$ ) (mol kg <sup>-1</sup> )	Temp. (K)					
		293.15		303.15		313.15	
		10 <sup>-3</sup> . $\rho$ (kg m <sup>-3</sup> )	10 <sup>6</sup> . $V_\phi$ (m <sup>3</sup> mol <sup>-1</sup> )	10 <sup>-3</sup> . $\rho$ (kg m <sup>-3</sup> )	10 <sup>6</sup> . $V_\phi$ (m <sup>3</sup> mol <sup>-1</sup> )	10 <sup>-3</sup> . $\rho$ (kg m <sup>-3</sup> )	10 <sup>6</sup> . $V_\phi$ (m <sup>3</sup> mol <sup>-1</sup> )
Mixed solvent system : 0% DMSO + water							
Glucose	0.0000	0.9982	-	0.9957	-	0.9922	-
	0.2047	1.0128	109.70	1.0104	111.32	1.0070	111.72
	0.4180	1.0289	106.30	1.0261	110.43	1.0230	110.24
	0.6398	1.0458	103.80	1.0431	109.31	1.0403	112.34
	0.8689	1.0649	100.10	1.0621	107.19	1.0589	107.26
	1.1059	1.0844	97.20	1.0824	105.35	1.0792	105.54
	1.3500	1.1051	94.39	1.1037	103.78	1.1011	103.63
	1.5992	1.1277	91.10	1.1262	102.24	1.1237	101.99
	1.8539	1.1513	87.90	1.1503	100.52	1.1480	100.26
	2.1174	1.1744	85.50	1.1759	98.87	1.1751	98.15
	2.3805	1.2005	82.50	1.2003	97.74	1.2044	95.46
Mixed solvent system : 10% DMSO + water							
	0.0000	1.0103	-	1.0062	-	1.0021	-
	0.2025	1.0236	112.56	1.0194	113.39	1.0152	114.47
	0.4147	1.0366	113.29	1.0324	113.91	1.0280	115.10
	0.6374	1.0494	113.91	1.0452	114.56	1.0406	115.73
	0.8718	1.0618	114.63	1.0576	115.22	1.0529	116.36
	1.1187	1.0740	115.26	1.0697	115.98	1.0651	116.95
	1.3798	1.0859	115.97	1.0815	116.68	1.0769	117.58
	1.6568	1.0972	116.89	1.0931	117.39	1.0883	118.36
	1.9509	1.1084	117.66	1.1043	118.10	1.0994	119.09
	2.2660	1.1186	118.76	1.1151	118.95	1.1098	120.06
	2.6035	1.1285	119.82	1.1250	120.04	1.1199	121.03

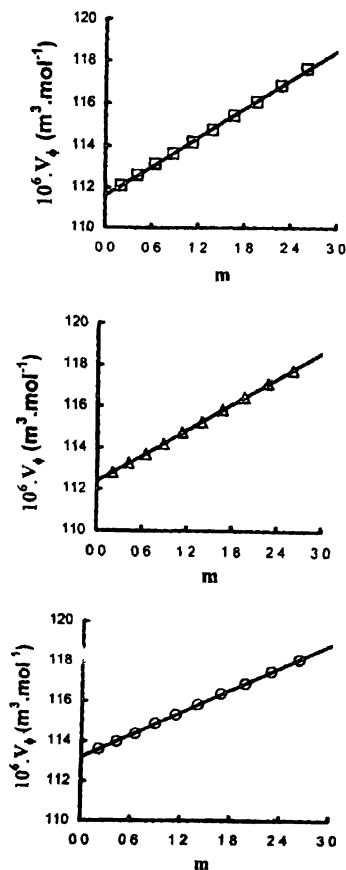


Fig. 1. Variation of  $V_\phi$  with  $m$  for aqueous solutions of glucose at different temperatures ( $\square$ ) 293.15 K, ( $\Delta$ ) 303.15 K, ( $\circ$ ) 313.15 K.

by computerized least square fitting of  $V_\phi$  versus  $m$  data to the above eq. (2) and the representative data in respect of glucose and sucrose are listed in Table 2 along with standard errors (given in parentheses).

The larger and positive values of  $V_\phi^0$  for glucose, fructose, sucrose and maltose in water as well as in the presence of (DMSO + water) mixed solvent systems indicate the presence of strong solute-solvent interactions. Further, there is an increase in the values of  $V_\phi^0$  with the increasing percentage of DMSO in (DMSO + water) mixed solvent systems. This shows that the strength of solute-solvent interactions increases with the increasing amount of DMSO in (DMSO + water) mixed solvent systems. On perusing the values of  $S_v$ , it is seen that these are very small in comparison with those of  $V_\phi^0$ , thereby showing the presence of weak solute-solute interactions in solutions of glucose, fructose, sucrose and maltose in water as well as in (DMSO + water) mixed solvent systems.

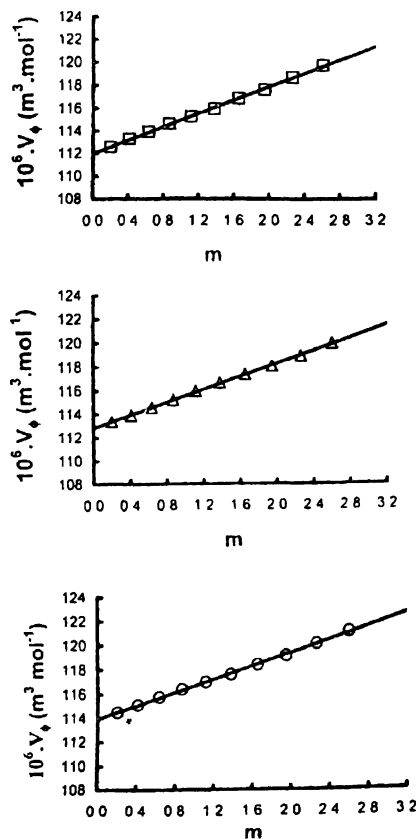


Fig. 2. Variation of  $V_\phi$  with  $m$  for solutions of glucose in 10% (DMSO + water) mixed solvent system at different temperatures ( $\square$ ) 293.15 K, ( $\Delta$ ) 303.15 K, ( $\circ$ ) 313.15 K.

*Partial molar volumes of transfer ( $V_{2,tr}^0$ ) for mono- and disaccharides from water to (DMSO + water) mixed solvent systems :*

Partial molar volumes of transfer for mono- and disaccharides from water to (DMSO + water) mixed solvent systems at different temperatures have been obtained from the following equation,

$$V_{2,tr}^0 = [V_2^0\{(DMSO + water)\} - V_2^0(water)] \quad (3)$$

The results are presented in Table 3. A perusal of Table 3 shows that in each case the values of  $V_{2,tr}^0$  are positive and are rendered more positive with the increasing content of DMSO in (DMSO + water) mixed solvent systems. The positive values of  $V_{2,tr}^0$  may be explained in the light of different models<sup>10,11</sup>. Partial molar volume ( $V_2^0$ ) of a non-electrolyte at infinite dilution is a combination of the intrinsic volume ( $V_{int}$ ) of the non-electrolyte and volume due to its interaction with solvent ( $V_s$ ) which was further modified later as<sup>11</sup>,

**Table 2.** Values of limiting apparent molar volume ( $V_\phi^0$ ) and experimental slope ( $S_\phi$ ) for mono- and disaccharides in water and in (DMSO + water) mixed solvent systems of varying composition at different temperatures

Saccharides	$10^6 \cdot V_\phi^0$ ( $\text{m}^3 \text{mol}^{-1}$ )				$10^6 \cdot S_\phi$ ( $\text{m}^3 \text{kg mol}^{-2}$ )			
	Water	10% DMSO	20% DMSO	30% DMSO	Water	10% DMSO	20% DMSO	30% DMSO
Glucose	111.60 ( $\pm 0.02$ )	111.98 ( $\pm 0.13$ )	112.89 ( $\pm 0.13$ )	113.71 ( $\pm 0.13$ )	2.30 ( $\pm 0.04$ )	2.97 ( $\pm 0.39$ )	3.20 ( $\pm 0.42$ )	3.40 ( $\pm 0.45$ )
Glucose	112.40 ( $\pm 0.01$ )	112.83 ( $\pm 0.13$ )	113.90 ( $\pm 0.13$ )	114.83 ( $\pm 0.13$ )	2.05 ( $\pm 0.02$ )	2.74 ( $\pm 0.36$ )	3.06 ( $\pm 0.40$ )	3.27 ( $\pm 0.43$ )
Glucose	113.22 ( $\pm 0.01$ )	113.96 ( $\pm 0.13$ )	114.95 ( $\pm 0.13$ )	115.98 ( $\pm 0.13$ )	1.89 ( $\pm 0.02$ )	2.68 ( $\pm 0.35$ )	2.82 ( $\pm 0.37$ )	3.03 ( $\pm 0.39$ )

Standard errors are given in parentheses.

**Table 3.** Partial molar volumes of transfer ( $V_{2,tr}^0$ ) for mono- and disaccharides from water to (DMSO + water) mixed solvent systems of varying composition at different temperatures

Saccharides	$10^6 \cdot V_{2,tr}^0$ ( $\text{m}^3 \text{mol}^{-1}$ )		
	10% DMSO	20% DMSO	30% DMSO
Temp. : 293.15 K			
Glucose	0.38	1.29	2.11
Fructose	0.44	1.42	2.50
Sucrose	0.43	1.42	2.43
Maltose	1.53	2.53	3.54
Temp. : 303.15 K			
Glucose	0.43	1.50	2.17
Fructose	0.63	1.61	2.45
Sucrose	0.59	1.59	2.44
Maltose	1.62	2.59	3.40
Temp. : 313.15 K			
Glucose	0.74	1.73	2.76
Fructose	0.88	1.89	2.95
Sucrose	0.42	1.42	2.36
Maltose	1.43	2.36	3.41

$$V_2^0 = V_{v,w} + V_{\text{void}} - V_{\text{shrinkage}} \quad (4)$$

where  $V_{v,w}$  is the Van der Waals volume,  $V_{\text{void}}$  is the associated void<sup>12</sup> or empty volume and  $V_{\text{shrinkage}}$  is the volume of shrinkage. It has been assumed that  $V_{v,w}$  and  $V_{\text{void}}$  have the same magnitude in water and in (DMSO +

water) mixed solvent systems. Therefore, the positive values of  $V_{2,tr}^0$  from water to (DMSO + water) mixed solvent systems can be attributed to the decrease in the volume of shrinkage because of stronger interactions between DMSO and hydroxyl groups of glucose, fructose, sucrose and maltose. Furthermore, these interactions will reduce the structure-breaking effect of DMSO on water. In other words, more water is released as bulk water in the presence of mono- and disaccharides. Since bulk water has higher volume contribution than structure-broken water, therefore this factor will also contribute to positive value of  $V_{2,tr}^0$  observed in the present study.

*Densities and viscosities of solutions of mono- and disaccharides as a function of molality (m) in (DMSO + water) mixed solvent systems at different temperatures :*

The densities ( $\rho$ ) and viscosities ( $\eta$ ) of the solutions of mono- and disaccharides have been determined at different temperatures (293.15, 303.15 and 313.15 K) as a function of concentration (molality,  $m$ ) in (DMSO + water) mixed solvent systems of different compositions i.e. 0, 10, 20 and 30% (w/w). The representative data in respect of glucose are presented in Table 4.

The viscosity-concentration data have been analysed in the light of the Jones-Dole equation,

$$\frac{\eta}{\eta_0} = \eta_{\text{rel}} = 1 + A\sqrt{C} + BC \quad (5)$$

On expressing concentration in terms of molality ( $m$ ), eq.

**Table 4.** Densities ( $\rho$ ) and viscosities ( $\eta$ ) of solutions of mono- and disaccharides as a function of molality ( $m$ ) in (DMSO + water) mixed solvent systems at different temperatures

Saccharides	Molality ( $m$ ) ( $\text{mol kg}^{-1}$ )	Temp. (K)								
		293.15			303.15			313.15		
		$10^{-3} \cdot \rho$ ( $\text{kg m}^{-3}$ )	$\eta$ ( $\text{mPa.s}$ )	$\frac{(\eta_{\text{rel}} - 1)}{\sqrt{m}}$	$10^{-3} \cdot \rho$ ( $\text{kg m}^{-3}$ )	$\eta$ ( $\text{mPa.s}$ )	$\frac{(\eta_{\text{rel}} - 1)}{\sqrt{m}}$	$10^{-3} \cdot \rho$ ( $\text{kg m}^{-3}$ )	$\eta$ ( $\text{mPa.s}$ )	$\frac{(\eta_{\text{rel}} - 1)}{\sqrt{m}}$
Mixed solvent systems : 0% DMSO + water										
Glucose	0.0000	0.9982	1.0020	-	0.9957	0.7977	-	0.9922	0.6532	-
	0.2047	1.0128	1.0181	0.0355	1.0104	0.8099	0.0334	1.0070	0.6473	-0.0198
	0.4180	1.0289	1.0939	0.1418	1.0261	0.8856	0.1662	1.0230	0.7501	0.2232
	0.6398	1.0458	1.2513	0.3110	1.0431	0.9965	0.3001	1.0403	0.8619	0.3739
	0.8689	1.0649	1.4068	0.4334	1.0621	1.1182	0.4102	1.0589	0.9915	0.5278
	1.1059	1.0844	1.5907	0.5586	1.0824	1.2512	0.5081	1.0792	1.1160	0.6319
	1.3500	1.1051	1.7658	0.6561	1.1037	1.4039	0.6067	1.1011	1.2599	0.7404
	1.5992	1.1277	1.9660	0.7608	1.1262	1.5597	0.6915	1.1237	1.3938	0.8195
	1.8539	1.1513	2.1620	0.8503	1.1503	1.7251	0.7715	1.1480	1.5273	0.8868
	2.1174	1.1744	2.3544	0.9275	1.1759	1.9081	0.8526	1.1751	1.6889	0.9707
2.3805	1.2005	2.5589	1.0070	1.2003	2.0777	0.9134	1.2044	1.8233	1.0225	

Table-4 (contd.)

Mixed solvent systems : 10% DMSO + water									
0.0000	1.0103	0.8854	-	1.0062	0.7016	-	1.0021	0.5761	-
0.2025	1.0236	0.9123	-0.1990	1.0194	0.7076	-0.2510	1.0152	0.5474	-0.3600
0.4147	1.0366	0.9930	-0.0140	1.0324	0.7684	-0.0570	1.0280	0.5872	-0.1570
0.6374	1.0494	1.1180	0.1450	1.0452	0.8563	0.0920	1.0406	0.6600	0.0130
0.8718	1.0618	1.2552	0.2707	1.0576	0.9779	0.2420	1.0529	0.7630	0.1800
1.1187	1.0740	1.4076	0.3827	1.0697	1.1166	0.3780	1.0651	0.8653	0.3070
1.3798	1.0859	1.5905	0.5000	1.0815	1.2550	0.4880	1.0769	0.9885	0.4370
1.6568	1.0972	1.8048	0.6224	1.0931	1.4518	0.6370	1.0883	1.1358	0.5740
1.9509	1.1084	2.0741	0.7660	1.1043	1.6456	0.7610	1.0994	1.2900	0.6980
2.2660	1.1186	2.3474	0.8920	1.1151	1.8352	0.8640	1.1098	1.4546	0.8150
2.6035	1.1285	2.6462	1.0170	1.1250	2.0604	0.9810	1.1199	1.6155	0.9130
Mixed solvent systems : 20% DMSO + water									
0.0000	1.0137	0.8674	-	1.0108	0.6775	-	1.0038	0.5422	-
0.2019	1.0267	0.8912	-0.2460	1.0237	0.6848	-0.3150	1.0166	0.5379	-0.3930
0.4135	1.0394	0.9737	-0.0440	1.0363	0.7285	-0.1350	1.0292	0.5709	-0.1960
0.6357	1.0519	1.0778	0.0949	1.0486	0.8301	0.0510	1.0416	0.6438	-0.0180
0.8697	1.0639	1.2082	0.2207	1.0607	0.9346	0.1840	1.0537	0.7306	0.1270
1.1166	1.0758	1.3892	0.3657	1.0724	1.0590	0.3100	1.0654	0.8368	0.2660
1.3775	1.0873	1.5712	0.4840	1.0838	1.2125	0.4430	1.0769	0.9583	0.3980
1.6547	1.0983	1.7973	0.6179	1.0949	1.3887	0.5760	1.0879	1.1103	0.5440
1.9496	1.1089	2.0597	0.7560	1.1052	1.5651	0.6890	1.0986	1.2816	0.6890
2.2659	1.1187	2.3308	0.8810	1.1151	1.7847	0.8220	1.1088	1.4477	0.8080
2.6056	1.1279	2.6404	1.0130	1.1246	2.0274	0.9550	1.1185	0.6369	0.9330
Mixed solvent systems : 30% DMSO + water									
0.0000	1.0143	0.8384	-	1.0116	0.6497	-	1.0082	0.5176	-
0.2018	1.0271	0.8490	-0.3400	1.0243	0.6687	-0.3600	1.0207	0.5250	-0.4370
0.4134	1.0396	0.9421	-0.0930	1.0367	0.7085	-0.1740	1.0330	0.5566	-0.2300
0.6357	1.0519	1.0560	0.0676	1.0487	0.8053	0.0120	1.0450	0.6240	-0.0560
0.8699	1.0638	1.1814	0.1920	1.0605	0.9167	0.1600	1.0567	0.7141	0.1000
1.1172	1.0753	1.3451	0.3240	1.0719	1.0464	0.2950	1.0681	0.8327	0.2600
1.3790	1.0864	1.5150	0.4360	1.0829	1.1996	0.4290	1.0791	0.9447	0.3800
1.6574	1.0969	1.7352	0.5684	1.0935	1.3831	0.5700	1.0897	1.0854	0.5140
1.9538	1.1072	1.9824	0.7000	1.1037	1.5581	0.6820	1.1001	1.2229	0.6240
2.2715	1.1167	2.2585	0.8320	1.1134	1.7595	0.8000	1.1096	1.4296	0.7886
2.6124	1.1259	2.5745	0.9710	1.1224	1.9735	0.9120	1.1184	1.6319	0.9270

(5) takes up the following form<sup>13</sup>,

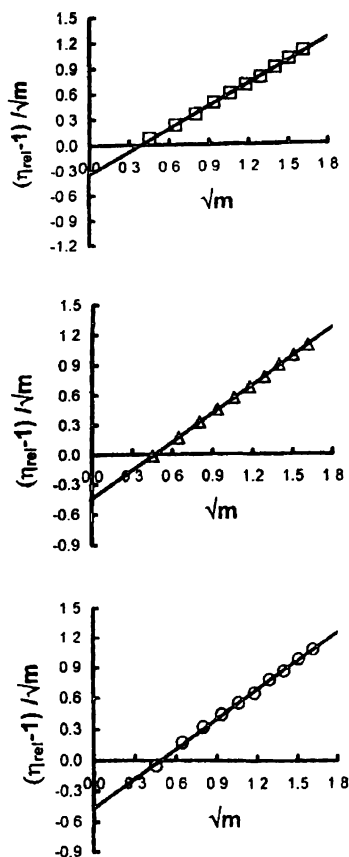
$$\frac{\eta}{\eta_0} = \eta_{rel} = 1 + A\sqrt{m} + Bm \quad (6)$$

or

$$\frac{(\eta_{rel} - 1)}{\sqrt{m}} = A + B\sqrt{m} \quad (7)$$

In the above eq. (7), the coefficients *A* and *B* are the

measure of solute-solute and solute-solvent interactions<sup>14</sup> respectively. From eq. (7) it follows that the plots of  $(\eta_{rel} - 1)/\sqrt{m}$  versus  $\sqrt{m}$  should be linear. This has actually been found in the present study. These linear plots have been presented in representative Figs. 3, 4. The values of coefficients *A* and *B* have been determined by computerized least square fitting of  $(\eta_{rel} - 1)/\sqrt{m}$  versus  $\sqrt{m}$  data to eq. (7), and are listed in Table 5 along



**Fig. 3.** Variation of  $(\eta_{rel} - 1)/\sqrt{m}$  with  $\sqrt{m}$  for aqueous solutions of glucose at different temperatures : (□) 293.15 K; (Δ) 303.15 K; (○) 313.15 K.

with the standard errors (given in parentheses). It is seen that the values of  $A$  for mono- and disaccharides in 0% (DMSO + water) i.e. in purely aqueous solutions (water) are negative. The same is true in the case of (DMSO + water) mixed solvent systems of varying composition. Further, a perusal of Table 5 shows that the values of  $A$  are rendered increasingly more negative with increasing percentage of DMSO in (DMSO + water) mixed solvent systems at different temperatures. This indicates that in purely aqueous solutions, i.e. in water, the solute-solute interactions are weak and that these are further weakened with the increasing percentage of DMSO in (DMSO + water) mixed solvent systems. On the other hand, the values of coefficient  $B$  are larger and positive in water as well as in (DMSO + water) mixed solvent systems of varying composition. This shows the presence of strong solute-solvent interactions in solutions of glucose, fructose, sucrose and maltose in purely aqueous medium as well as in (DMSO + water) mixed solvent systems of

varying composition. The larger positive values of  $B$  also indicate<sup>14-16</sup> that these mono- and disaccharides behaves as structure-makers in water as well as in (DMSO + water) mixed solvent systems of varying composition.

*Determination of limiting apparent molar expansibilities ( $\phi_E^0$ ) and the derivative  $(\partial^2 V_\phi^0/\partial T^2)_p$  from the temperature dependence of  $V_\phi^0$  :*

The variation of  $V_\phi^0$  with the temperature can be expressed<sup>17,18</sup> as below :

$$V_\phi^0 = a_0 + a_1 T + a_2 T^2 \quad (8)$$

The values of coefficients  $a_0$ ,  $a_1$  and  $a_2$  have been calculated from eq. (8) and are listed in Table 6.

The limiting apparent molar expansibilities ( $\phi_E^0$ ) have been calculated<sup>17</sup> from the following relation,

$$\phi_E^0 = \left( \frac{\partial V_\phi^0}{\partial T} \right)_p = a_1 + 2a_2 T \quad (9)$$

The values of  $\phi_E^0$  for glucose, fructose, sucrose and maltose at different temperatures in (DMSO + water) mixed solvent systems of varying composition are presented in Table 7. A perusal of Table 7 shows that  $\phi_E^0$  tends to increase with rise in temperature. The increased values of  $\phi_E^0$  at elevated temperatures may be attributed<sup>19</sup> to the structure making capacity of these mono- and disaccharides.

Hepler<sup>20</sup> has proposed a method, by which qualitative information on solvation of solutes can be obtained from thermal expansion of the solution by the following relation,

$$\left( \frac{\partial C_p^0}{\partial T} \right)_T = -T \left( \frac{\partial^2 V_\phi^0}{\partial T^2} \right)_p \quad (10)$$

According to this, the left hand side of the above equation should be positive for all structure breaking solutes and therefore, structure-breaking solutes possess negative value of  $(\partial^2 V_\phi^0/\partial T^2)_p$ . On the other hand, positive value of  $(\partial^2 V_\phi^0/\partial T^2)_p$  should be associated with structure-making solutes. In the present study the values of  $(\partial^2 V_\phi^0/\partial T^2)_p$  have been obtained from eq. (8) and are listed in Table 8. It is seen that values of  $(\partial^2 V_\phi^0/\partial T^2)_p$  for glucose, fructose, sucrose and maltose are positive in purely aqueous medium (water) and in (DMSO + water) mixed solvents systems of varying composition. The positive values of  $(\partial^2 V_\phi^0/\partial T^2)_p$  suggest that these mono- and disaccharides behave as structure-makers in purely aqueous medium (water) as well as in the above mentioned mixed

**Table 5.** Values of coefficients *A* and *B* of Jones-Dole equation for mono- and disaccharides in water and in (DMSO + water) mixed solvent systems of varying composition at different temperatures

Saccharides	A (kg <sup>1/2</sup> mol <sup>-1/2</sup> )				B (kg mol <sup>-1</sup> )			
	Water		30% DMSO		Water		30% DMSO	
	10% DMSO	20% DMSO	20% DMSO	30% DMSO	10% DMSO	20% DMSO	20% DMSO	30% DMSO
	Temp. : 293.15 K							
Glucose	-0.34 (±0.12)	-0.69 (±0.10)	-0.76 (±0.16)	-0.82 (±0.13)	0.88 (±0.05)	1.04 (±0.05)	1.08 (±0.08)	1.09 (±0.06)
Fructose	-0.42 (±0.11)	-0.75 (±0.12)	-0.79 (±0.13)	-0.84 (±0.13)	0.92 (±0.05)	1.06 (±0.06)	1.09 (±0.06)	1.10 (±0.07)
Sucrose	-0.45 (±0.22)	-0.80 (±0.24)	-0.86 (±0.22)	-0.92 (±0.17)	0.99 (±0.09)	1.11 (±0.11)	1.12 (±0.11)	1.14 (±0.09)
Maltose	-0.47 (±0.15)	-0.84 (±0.22)	-0.88 (±0.18)	-0.95 (±0.19)	1.02 (±0.06)	1.13 (±0.08)	1.14 (±0.12)	1.15 (±0.09)
	Temp. : 303.15 K							
Glucose	-0.44 (±0.14)	-0.75 (±0.12)	-0.83 (±0.17)	-0.87 (±0.14)	0.94 (±0.06)	1.07 (±0.06)	1.09 (±0.09)	1.10 (±0.07)
Fructose	-0.49 (±0.18)	-0.79 (±0.12)	-0.86 (±0.16)	-0.90 (±0.10)	0.98 (±0.08)	1.10 (±0.06)	1.13 (±0.06)	1.13 (±0.06)
Sucrose	-0.50 (±0.21)	-0.85 (±0.21)	-0.94 (±0.24)	-0.97 (±0.20)	1.02 (±0.09)	1.13 (±0.10)	1.16 (±0.12)	1.16 (±0.10)
Maltose	-0.53 (±0.21)	-0.87 (±0.19)	-0.97 (±0.22)	-1.00 (±0.20)	1.04 (±0.09)	1.11 (±0.09)	1.18 (±0.10)	1.19 (±0.10)
	Temp. : 313.15 K							
Glucose	-0.44 (±0.15)	-0.87 (±0.14)	-0.93 (±0.16)	-0.98 (±0.12)	0.97 (±0.07)	1.11 (±0.07)	1.15 (±0.09)	1.16 (±0.07)
Fructose	-0.52 (±0.16)	-0.88 (±0.12)	-0.96 (±0.14)	-0.99 (±0.10)	1.00 (±0.07)	1.13 (±0.06)	1.16 (±0.06)	1.18 (±0.06)
Sucrose	-0.54 (±0.20)	-0.92 (±0.23)	-0.99 (±0.22)	-1.02 (±0.18)	1.04 (±0.09)	1.14 (±0.11)	1.18 (±0.11)	1.18 (±0.09)
Maltose	-0.62 (±0.21)	-0.97 (±0.25)	-1.01 (±0.25)	-1.06 (±0.26)	1.07 (±0.09)	1.16 (±0.12)	1.19 (±0.11)	1.20 (±0.13)

Standard errors are given in parentheses.

**Table 6.** Values of coefficients *a*<sub>1</sub> for mono- and disaccharides in water and in (DMSO + water) mixed solvent systems of varying composition

Saccharides	Water				10% DMSO				20% DMSO				30% DMSO						
	10 <sup>5</sup> .a <sub>0</sub> (m <sup>3</sup> mol <sup>-1</sup> )		10 <sup>8</sup> .a <sub>1</sub> (m <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )		10 <sup>10</sup> .a <sub>2</sub> (m <sup>3</sup> mol <sup>-1</sup> K <sup>-2</sup> )		10 <sup>5</sup> .a <sub>0</sub> (m <sup>3</sup> mol <sup>-1</sup> )		10 <sup>8</sup> .a <sub>1</sub> (m <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )		10 <sup>10</sup> .a <sub>2</sub> (m <sup>3</sup> mol <sup>-1</sup> K <sup>-2</sup> )		10 <sup>5</sup> .a <sub>0</sub> (m <sup>3</sup> mol <sup>-1</sup> )		10 <sup>8</sup> .a <sub>1</sub> (m <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )		10 <sup>10</sup> .a <sub>2</sub> (m <sup>3</sup> mol <sup>-1</sup> K <sup>-2</sup> )		
	9.10	2.04	1.00	24.00	21.15	-74.98	14.00	10.11	-1.83	2.00	9.42	2.26	1.50	15.27	-35.22	7.50	24.47	-29.56	8.00
Glucose	9.10	2.04	1.00	24.00	21.15	-74.98	14.00	10.11	-1.83	2.00	9.42	2.26	1.50	15.27	-35.22	7.50	24.47	-29.56	8.00
Fructose	30.10	-13.50	24.00	22.00	10.03	-1.93	2.00	11.46	-10.87	3.50	15.27	-35.22	7.50	24.47	-29.56	8.00	27.17	-35.52	7.50
Sucrose	38.36	-123.19	22.00	22.00	22.32	-17.03	4.50	19.34	3.74	1.00	24.47	-29.56	8.00	27.17	-35.52	7.50	27.17	-35.52	7.50
Maltose	38.13	-110.76	20.00	20.00	25.57	-26.38	6.00	24.37	-17.53	4.50	27.17	-35.52	7.50	27.17	-35.52	7.50	27.17	-35.52	7.50



**Table 7.** Limiting apparent molar expansibility ( $\phi_E^0$ ) for mono- and disaccharides in aqueous solutions and in (DMSO + water) mixed solvent systems at different temperatures

Saccharides	$10^6 \cdot \phi_E^0$ ( $m^3 \text{ mol}^{-1} \text{ K}^{-1}$ )											
	Water			10% DMSO			20% DMSO			30% DMSO		
	293.15K	303.15K	313.15K	293.15K	303.15K	313.15K	293.15K	303.15K	313.15K	293.15K	303.15K	313.15K
Glucose	0.079	0.081	0.083	0.071	0.099	0.127	0.099	0.103	0.107	0.111	0.114	0.117
Fructose	0.057	0.105	0.153	0.098	0.102	0.106	0.097	0.104	0.111	0.088	0.103	0.118
Sucrose	0.058	0.102	0.146	0.094	0.103	0.112	0.096	0.098	0.100	0.086	0.099	0.111
Maltose	0.065	0.105	0.145	0.088	0.099	0.109	0.089	0.097	0.105	0.085	0.100	0.115

**Table 8.** Values of  $(\partial^2 V_\phi^0 / \partial T^2)_p$  for mono- and disaccharides in water and in (DMSO + water) mixed solvent systems

Saccharides	$10^{10} \cdot (\partial^2 V_\phi^0 / \partial T^2)_p$ ( $m^6 \text{ mol}^{-1} \text{ K}^{-2}$ )			
	Water	10% DMSO	20% DMSO	30% DMSO
Glucose	2.00	28.00	4.00	3.00
Fructose	48.00	4.00	7.00	15.00
Sucrose	44.00	9.00	2.00	13.00
Maltose	40.00	12.00	9.00	15.00

solvent systems.

The activation thermodynamic quantities ( $\Delta\mu_2^{0\#}$ ,  $\Delta S_2^{0\#}$  and  $\Delta H_2^{0\#}$ ) of viscous flow for mono- and disaccharides in (DMSO + water) mixed solvent systems of varying composition :

The free energies of activation of viscous flow,  $\Delta\mu_1^{0\#}$  and  $\Delta\mu_2^{0\#}$  per mole of solvent and solute respectively have been calculated as below :

The coefficient  $B$  of the Jones-Dole equation is related to the free energy of activation by the following equation<sup>21</sup>,

$$B = \frac{V_1^0 - V_2^0}{1000} + \frac{V_1^0}{1000} \left[ \frac{\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}}{RT} \right] \quad (11)$$

where  $V_1^0$  and  $V_2^0$  are the partial volumes of the solvent and solute respectively.  $\Delta\mu_1^{0\#}$  is the free energy of activation per mole of solvent and  $\Delta\mu_2^{0\#}$  is the free energy of activation per mole of solute. The values of  $\Delta\mu_1^{0\#}$  and  $\Delta\mu_2^{0\#}$  are calculated using the following equations<sup>22</sup>,

$$\Delta\mu_1^{0\#} = RT \ln \left[ \frac{\eta_0 V_1^0}{hN} \right] \quad (12)$$

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + \frac{RT}{V_1^0} [1000B - (V_1^0 - V_2^0)] \quad (13)$$

where  $h$  is the Plank's constant,  $N$  the Avogadro number,  $R$  the gas constant and  $T$  the absolute temperature.

The entropy of activation ( $\Delta S_2^{0\#}$ ) of viscous flow has been obtained from the following relation<sup>21</sup>,

$$\frac{d(\Delta\mu_2^{0\#})}{dT} = -\Delta S_2^{0\#} \quad (14)$$

The enthalpy of activation ( $\Delta H_2^{0\#}$ ) of viscous flow has been calculated with the help of following relation<sup>21</sup>,

$$\Delta H_2^{0\#} = \Delta\mu_2^{0\#} + T\Delta S_2^{0\#} \quad (15)$$

The values of  $\Delta\mu_1^{0\#}$  and  $\Delta\mu_2^{0\#}$  at different temperatures have been presented in Tables 9 and 10 respectively. It is seen that the values of  $\Delta\mu_2^{0\#}$  for mono- and disaccharides in water and also in (DMSO + water) mixed solvent systems of varying composition, are larger as compared to those of  $\Delta\mu_1^{0\#}$  and that in each case  $(\Delta\mu_2^{0\#} - \Delta\mu_1^{0\#}) > 0$ . From this it is inferred that mono- and disaccharides behave as structure-makers<sup>21</sup> in water as well as in (DMSO + water) mixed solvent systems of varying composition.

The values of entropy and enthalpy of activation of viscous flow for mono- and disaccharides in water and in (DMSO + water) mixed solvent systems have been calculated at different temperatures and presented in Table 11. It is seen that values of both  $T\Delta S_2^{0\#}$  and  $\Delta H_2^{0\#}$  are positive in water but are negative in (DMSO + water)

**Table 9.** Free energy of activation of viscous flow,  $\Delta\mu_1^{0\#}$  for water and (DMSO + water) mixed solvent systems of varying composition at different temperatures

Solvent	$\Delta\mu_1^{0\#}$ ( $\text{kJ mol}^{-1}$ )		
	293.15 K	303.15 K	313.15 K
Water	9.195	8.976	8.713
10% DMSO + water	9.104	8.838	8.627
20% DMSO + water	9.316	9.018	8.752
30% DMSO + water	9.467	9.154	8.871

**Table 10.** Free energy of activation of viscous flow,  $\Delta\mu_2^{0\#}$  for mono- and disaccharides in water and in (DMSO + water) mixed solvent systems of varying composition at different temperatures

Solvent	$\Delta\mu_2^{0\#}$ (kJ mol <sup>-1</sup> )		
	293.15 K	303.15 K	313.15 K
	Glucose		
Water	145.81	153.12	160.58
10% DMSO + water	155.20	163.65	173.77
20% DMSO + water	144.99	150.48	161.47
30% DMSO + water	134.03	139.37	149.36
	Fructose		
Water	145.81	153.12	160.58
10% DMSO + water	158.47	167.47	176.15
20% DMSO + water	145.70	153.53	163.50
30% DMSO + water	135.28	141.73	150.93
	Sucrose		
Water	145.81	153.12	160.58
10% DMSO + water	177.32	185.27	192.53
20% DMSO + water	161.95	170.33	176.82
30% DMSO + water	149.81	156.38	162.61
	Maltose		
Water	145.81	153.12	160.58
10% DMSO + water	182.05	189.70	195.93
20% DMSO + water	165.20	174.60	180.45
30% DMSO + water	152.76	160.98	166.38

mixed solvent systems of varying composition. From the positive values of  $T\Delta S_2^{0\#}$  and  $\Delta H_2^{0\#}$  it follows that in purely aqueous solutions of mono- and disaccharides the transition state is associated with bond-breaking and a decrease in order<sup>21</sup>. This suggests that the slip-plane is somewhere in the region of centro-symmetric order. On the other hand, the negative values of  $T\Delta S_2^{0\#}$  and  $\Delta H_2^{0\#}$  in (DMSO + water) mixed solvent systems show that the formation of the transition state is associated with bond-making and an increase in order<sup>21</sup>. This suggests that slip-plane is in the disordered region.

### Experimental

Glucose, fructose, sucrose and maltose were of analytical reagents grade of 99.9 mol % purity and were used as such. The reagents were always paced in a desiccator over P<sub>2</sub>O<sub>5</sub> to keep them in dry atmosphere.

Freshly doubly distilled water (sp. cond.  $\sim 10^{-6}$   $\Omega^{-1}$  cm<sup>-1</sup>) was used for preparing the binary mixed solvent systems of dimethyl sulphoxide (DMSO) + water of different compositions viz. 10, 20 and 30%, (w/w). Solutions were prepared in these solvent systems on molality (*m*) scale using an electronic balance (Mettler) having an accuracy of  $\pm 1.0 \times 10^{-4}$  g.

Densities of the mixed solvent systems and solutions of mono- and disaccharides were measured at different temperatures (293.15, 303.15 and 313.15  $\pm$  0.01 K) us-

**Table 11.** Values of  $T\Delta S_2^{0\#}$  and  $\Delta H_2^{0\#}$  for mono- and disaccharides in water and in (DMSO + water) mixed solvent systems of varying composition at different temperatures

Mixed solvent systems	$T\Delta S_2^{0\#}$ (kJ mol <sup>-1</sup> )			$\Delta H_2^{0\#}$ (kJ mol <sup>-1</sup> )		
	293.15 K	303.15 K	313.15 K	293.15 K	303.15 K	313.15 K
	Glucose					
Water	62.83	67.19	71.69	208.63	220.30	232.27
10% DMSO + water	-212.21	-281.50	-290.78	-117.01	-117.85	-117.01
20% DMSO + water	-241.57	-249.81	-258.05	-96.58	-99.33	-96.58
30% DMSO + water	-224.72	-232.39	-240.06	-90.69	-93.02	-90.69
	Fructose					
Water	62.83	67.19	71.69	208.63	220.30	232.27
10% DMSO + water	-259.16	-268.00	-276.84	-100.69	-100.53	-100.69
20% DMSO + water	-260.90	-269.80	-278.70	-115.20	-116.27	-115.20
30% DMSO + water	-229.42	-237.24	-245.07	-94.14	-95.51	-94.14
	Sucrose					
Water	62.83	67.19	71.69	208.63	220.30	232.27
10% DMSO + water	-222.93	-230.53	-238.14	-45.61	-45.26	-45.61
20% DMSO + water	-217.99	-225.43	-232.86	-56.05	-55.10	-56.05
30% DMSO + water	-187.65	-194.05	-200.45	-37.84	-37.67	-37.84

	Maltose					
Water	62.83	67.19	71.69	208.63	220.30	232.27
10% DMSO + water	-203.56	-210.50	-217.44	-21.51	-20.80	-21.51
20% DMSO + water	-223.51	-231.13	-238.76	-58.31	-56.53	-58.31
30% DMSO + water	-199.69	-206.50	-213.31	-46.93	-45.52	-46.93

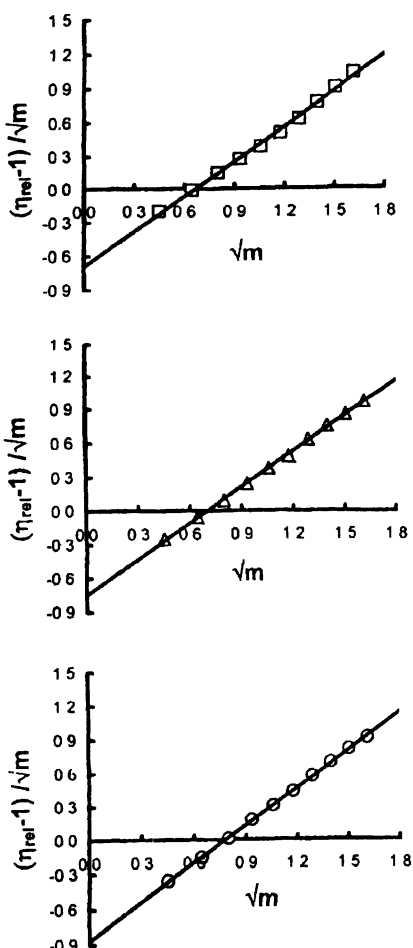


Fig. 4. Variation of  $(\eta_{rel} - 1)/\sqrt{m}$  with  $\sqrt{m}$  for aqueous solutions of glucose in 10% (DMSO + water) mixed solvent system at different temperatures : (□) 293.15 K; (Δ) 303.15 K; (○) 313.15 K.

ing a digital vibrating tube densimeter (Anton parr, Austria). Viscosities of the solutions were measured at the desired temperature using an Ostwald's suspended level type viscometer as per details described by Findlay<sup>23</sup>. Density and viscosity measurements were carried out in a thermostated bath, the temperature of which was maintained within  $\pm 0.01$  K of the desired values. The uncertainty of the viscosities was  $\pm 1 \times 10^{-4}$  mPa.s.

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