Monatshefte für Chemie 134, 797–809 (2003)
DOI 10.1007/s00706-002-0530-7

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Apparent Molar Volume and Viscosity Studies on Some Carbohydrates in Solutions

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Received March 19, 2002; accepted (revised) July 31, 2002

Summary. The apparent molar volume (ϕ_v) and viscosity (η) of *L*(+)-arabinose, *D*(+)-galactose, *D*(−)-fructose, *D*(+)-glucose, sucrose, lactose, and maltose in water and in 0.1% and 0.3% water-Surf Excel solutions were measured as a function of solute concentrations at 308.15, 313.15, and 323.15 K, respectively. The apparent molar volume (ϕ_v) of the carbohydrates was found to be a linear function of the concentration. From a ϕ_v versus molality (*b*) plot, the apparent molar volume at infinite dilution (ϕ_v°), which is practically equal to the partial molar volume at infinite dilutions ($\overline{V}_2^\circ$) of these substances was determined. The viscosity coefficients *B* and *D* for the carbohydrates were calculated on the basis of the viscosity of the solutions and the solvent using the *Jones-Dole* equation. The activation free energy for viscous flow ($\Delta G^{\neq}$) of the solutions was also calculated using the *Eyring* equation. The carbohydrates showed structure making behaviour both in water and in water-Surf Excel solutions. When water-Surf Excel solutions and pure water solutions containing carbohydrate molecules are compared, the former were found to be more structured. The behaviour of these solutes in water and in water-Surf Excel solution systems is discussed in the light of solute–solvent interactions.

Keywords. Apparent molar volume; Viscosity coefficient; Activation parameters; Hydrogen bonding.

Introduction

Surfactant molecules in water solutions at low concentration exist in monomeric form and behave like normal electrolytes or non-polar molecules. However, on increasing concentrations of the surfactant an abrupt change in several physico-chemical properties of the solution is observed. Typical examples of these properties are osmotic pressure, electrical conductance, surface tension, viscosity, and apparent molar volume. This behaviour of surfactant solutions is due to the formation of multi-molecular aggregates, called micelles [1]. Micelle formation is a typical hydrophobic process [2]. In water, surfactant molecules with their long hydrophobic tails undergo hydrophobic hydration. The concentration at which

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the micelle first appears is referred to as the critical micelle concentration (CMC). Above this concentration micelles are in dynamic equilibrium with the monomeric form of the surfactant in the bulk phase. Surfactants in water solutions generally form spherical micelles just above the CMC and associate further to form rod-like micelles at higher concentrations.

Carbohydrates play an important role in animal and plant life. Understanding of the behaviour of these molecules in water and in water-surfactant solution systems is of utmost importance in biological and pharmaceutical science. The hydration of carbohydrate is reported to depend on the percentage of axial and equatorial hydroxyl groups. It is more favourable when the hydroxyl group is in an equatorial position [3, 4]. Hydrogen bonding plays an important role in the interaction of components in water and in water-surfactant solution systems for polar non-electrolyte molecules. If a carbohydrate molecule is introduced into water and into water-surfactant solutions, the formation of carbohydrate-water and carbohydrate-surfactant hydrogen bonds will depend, to a large extent, on the spacing and orientations of the polar group of the carbohydrate molecules relative to the –OH geometry in water [5]. A large number of researchers [6–11] worked on such properties like apparent molar volumes, adiabatic compressibilities, specific heats etc. for carbohydrates in different concentration ranges. The results obtained by these studies differ for the same carbohydrate and thus the behaviour of carbohydrate molecules in solution systems can not be described conclusively. Although some volumetric and viscometric results on carbohydrate molecules in water alone are available, no volumetric and viscometric data are yet available for carbohydrate molecules in water-surfactant (Surf Excel) solution systems. Here, we report the effect of some carbohydrates on the structure of water and water-Surf Excel solution systems using the apparent molar volume and viscosity coefficient data. Commercial detergent, Surf Excel, is supposed to form micelles in water. Micelle formation forces water to be in a specific structural form depending on surfactant concentration and temperature. This forced structure (for surfactant) and the normal structure of water may be perturbed by the highly polar carbohydrate molecules. This perturbation is expected to affect the volumetric and viscometric properties to a high degree. This type of study on simple systems, sometimes, provides very useful information about the structure of many complex systems.

Results and Discussion

Carbohydrates are polyhydroxy aldehydes and ketones. Due to the presence of a large number of –OH groups, they are highly polar and are hydrated easily. The polarity of the carbohydrate molecules depends on the orientation of the hydroxyl groups in the molecule. The carbohydrates included in this study are *L*(+)-arabinose, *D*(+)-galactose, *D*(−)-fructose, and *D*(+)-glucose as monosaccharides and sucrose, lactose, and maltose as disaccharides.

The composition range for all carbohydrate systems were 0.20–1.00 $\mathrm{mol\,kg^{-1}}$. The concentration dependence of the apparent molar volumes (ϕ_v) in water and in 0.1% and 0.3% water Surf Excel solutions has been measured at the temperatures 308.15, 313.15, and 323.15 K. The data are tabulated in Table 1 and representative

Table 1. Apparent molar volumes (ϕ_v/cm^3 mol^{-1}) for *L*(+)-arabinose, *D*(+)-galactose, *D*(−)-fructose, *D*(+)-glucose, sucrose, lactose, and maltose in water, water – 0.1% SE, and water – 0.3% SE solutions at 308.15, 313.15, and 323.15 K

Molality (mol kg^{-1})	ϕ_v at 308.15 K							ϕ_v at 313.15 K							ϕ_v at 323.15 K						
	arabinose	galactose	fructose	glucose	sucrose	lactose	maltose	arabinose	galactose	fructose	glucose	sucrose	lactose	maltose	arabinose	galactose	fructose	glucose	sucrose	lactose	maltose
In water solution																					
0.2000	90.97	110.19	114.27	117.57	212.17	225.12	227.80	92.82	110.59	115.29	117.91	212.84	226.30	228.89	95.37	111.97	117.71	119.45	214.75	228.74	230.89
0.4000	92.85	110.74	114.99	118.01	212.93	226.17	228.89	95.44	111.17	116.12	118.3	213.39	227.25	229.98	97.28	112.55	118.10	119.97	215.30	229.51	231.96
0.6000	95.30	111.34	115.78	118.65	213.55	227.38	230.10	98.91	111.78	116.89	119.11	213.17	228.19	231.19	99.71	112.83	118.93	120.62	215.87	230.57	233.20
0.8000	95.20	111.86	116.51	119.30	214.21	228.25	230.98	99.13	112.38	117.67	119.79	214.72	229.21	232.21	99.83	113.39	119.62	121.20	216.57	231.52	234.15
1.0000	95.10	112.41	117.72	119.97	214.86	229.12	231.92	99.27	112.95	118.42	120.43	215.39	230.17	235.15	100.13	113.99	120.35	121.91	217.13	232.47	235.27
In water + 0.1% SE solution																					
0.2000	91.75	110.95	114.93	117.99	212.68	225.59	228.31	93.19	111.51	115.86	118.30	213.05	226.91	229.15	95.89	111.98	117.70	119.79	215.10	229.25	231.26
0.4000	94.57	110.59	115.65	118.63	213.44	226.62	229.27	96.23	112.10	116.59	118.92	213.73	227.89	230.27	98.26	112.57	118.43	120.43	215.90	230.19	232.32
0.6000	94.10	111.21	116.19	119.22	214.10	227.71	230.35	96.13	112.78	117.29	119.57	214.49	228.78	231.19	98.12	113.19	119.11	121.09	216.62	231.27	233.19
0.8000	93.89	111.87	116.92	119.87	214.85	228.65	231.41	95.79	113.41	117.92	120.19	215.22	229.93	232.21	97.69	113.85	119.82	121.72	217.32	232.31	234.37
1.0000	93.61	112.47	117.62	120.57	215.59	229.73	232.35	95.62	114.09	118.63	120.87	215.97	230.98	233.28	97.58	114.39	120.51	122.39	218.10	233.28	235.28
In water + 0.3% SE solution																					
0.2000	92.49	111.46	115.51	118.49	213.39	225.98	228.91	93.87	111.79	116.38	118.88	214.06	227.45	229.68	96.15	112.25	118.12	120.43	215.46	229.98	231.88
0.4000	95.10	112.05	116.13	119.12	213.20	226.93	229.89	96.91	112.43	117.05	118.51	213.87	228.39	230.71	98.78	112.89	118.85	121.09	215.13	231.01	232.78
0.6000	94.61	112.69	116.75	119.76	213.01	227.99	230.97	96.42	112.99	117.71	119.10	213.57	229.48	231.59	98.35	113.51	119.63	121.73	214.85	232.10	233.87
0.8000	93.99	113.41	117.40	120.41	213.17	229.05	232.05	96.05	116.63	118.32	119.73	213.99	230.42	232.65	97.90	114.12	120.29	122.32	215.43	233.05	234.88
1.0000	93.78	113.98	118.10	120.97	213.37	230.10	233.09	95.89	114.15	118.95	120.35	214.50	231.46	233.69	97.72	114.69	120.98	122.99	215.97	234.06	235.79

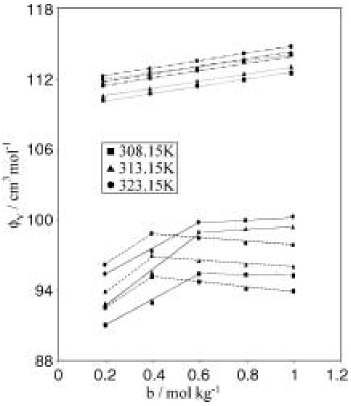

Fig. 1. Plots of apparent molar volumes (ϕ_v) versus molality for (a) arabinose (solid line) and galactose (dotted line) in water; (b) arabinose (dashed line) and galactose (dashed-dotted line) in water – 0.3% SE solutions at 308.15, 313.15, and 323.15 K

plots are shown in Fig. 1 (because of a very similar behaviour no plots are shown for the carbohydrates in 0.1% SE and for *D*(+)-glucose, *D*(−)-fructose, and maltose in water and in water – 0.3% SE solutions). It appears from Fig. 1 that ϕ_v is dependent on the carbohydrate concentration as well as on the temperature in water and in water-SE solvent systems. Plots of ϕ_v *vs*. molality of the carbohydrate molecules show a linear relationship except for *L*(+)-arabinose in water and in water-SE solvent systems and sucrose in 0.3% water-SE solvent systems. This relation also holds at higher temperature, the ϕ_v value is also found to be higher at least at the three chosen temperatures. The value of ϕ_v increases with the increase in molality of the carbohydrate suggesting that solute-solvent interactions increase with the increase in molality of the carbohydrates in solution. At a fixed Surf Excel concentration and temperature, the increase of ϕ_v with the concentration of added carbohydrates in the studied molality range (0.20–1.00 mol kg^{-1}) may be due to a change in micellar shape from roughly spheroidal aggregates to spherocylindrical aggregates. The ϕ_v of *L*(+)-arabinose in water and in 0.1% and 0.3% water-SE solvent systems rises initially, reaches a maximum and then decreases (Fig. 1). The molality at which the maximum value of ϕ_v is obtained (ϕ_{vm}) also depends on temperature. As the temperature rises, the value of ϕ_{vm} increases. From this it may be concluded that *L*(+)-arabinose has an optimum molality at which the structure making property reaches its maximum and after that the molality the solute behaves like a structure breaker. This is most probably due to strong solute–solute interactions at higher molality where the orientation of the molecule is restricted. The ϕ_v value of sucrose in 0.3% water-SE solution decreases with the increase in molality, reaches a minimum and then starts increasing again (Fig. 2). The initial decrease in ϕ_v may be attributed to the destruction of the tetrahedrally bonded water clusters and after attaining a minimum value, it starts increasing probably due to the stiffness of the concentrated solution.

The limiting apparent molar volume (ϕ_v°) which is taken to be the partial molar volume ($\overline{V}_2^\circ$) of the carbohydrates in water and in water-SE solutions at infinite dilution reflects the true volume of the solute and the volume change arising from

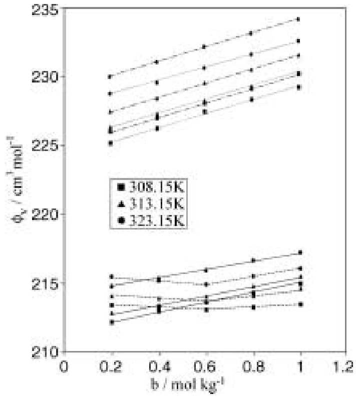

Fig. 2. Plots of apparent molar volumes (ϕ_v) versus molality for (a) sucrose (solid line) and lactose (dotted line) in water; (b) sucrose (dashed line) and lactose (dashed-dotted line) in water – 0.3% SE solutions at 308.15, 313.15, and 323.15 K

the solute–solvent interactions [12]. The ϕ_v° values are seen to increase with an increase in temperature (Table 2). The increase of ϕ_v° with temperature in water and in water-SE systems may be: (i) due to the increase in thermal energy at higher temperature, the relaxation to the bulk of the electrostricted water molecules from the interaction regions of –OH and –CH_2OH results in a positive volume change; (ii) that an increase in temperature renders the solute–solute interactions relatively weaker giving rise to a small negative volume change and (iii) the water–water interactions decreases with the increase in temperature leading to a small negative change in volume. The predominance of the positive contributions from (i) may overcome the small negative contribution from (ii) and (iii) and thus a net positive change in volume arises.

The value of ϕ_v° for all the carbohydrates studied are found to be higher in water-SE solutions than in pure water solutions. The variation of ϕ_v° with the concentration of SE can be rationalized in terms of the cosphere overlap model [13]. According to this model, the overlaps of the cospheres of two ions or polar groups and a polar group with that of a hydrophilic group always produces positive volume changes. On the other hand the overlap of the cosphere of a polar group with that of a hydrophobic group results in a negative volume change. Here, in the ternary systems, an overlap of the cosphere of SE–SE and SE-hydrophilic groups of carbohydrates takes place. The overlap of cosphere of SE gives a positive change in volume due to the relaxation of the electrostricted water molecules from its cosphere to the bulk. The overlap of the cospheres of SE with those of hydrophilic OH groups of carbohydrates results in a positive change of volume. The positive volume change due to overlap of the cospheres of SE with those of SE and the hydrophilic part of carbohydrates outweighs the negative volume change due to the overlap of hydrophobic parts of SE and carbohydrates giving greater ϕ_v° values in SE compared to that in water. The water–water and water-SE interactions are assumed to be the same and to produce no considerable change in volume. The change in ϕ_v° of an additive as a function of surfactant concentration and temperature may also reflect the change in its environment in the micellar systems. Higher

Table 2. Partial molar volumes at infinite dilution ($\phi_v^\circ \approx \overline{V}_2^\circ$), viscosity coefficients *B* and *D* for carbohydrate molecules in water, water – 0.1% SE, and water – 0.3% SE solutions at 308.15, 313.15, and 323.15 K

Carbohydrates	Solvent systems	$\phi_v^\circ/\mathrm{cm^3\,mol^{-1}}$ at			*B*-coefficient values at			*D*-coefficient values at		
		308.15 K	313.15 K	323.15 K	308.15 K	313.15 K	323.15 K	308.15 K	313.15 K	323.15 K
arabinose	H_2O	90.63	91.90	94.84	0.3665	0.3158	0.3128	– 0.4131	– 0.4835	– 0.1152
	$H_2O + 0.1\%$ SE	92.67	94.07	96.67	0.3910	0.3064	0.2934	– 1.7796	0.6487	0.6551
	$H_2O + 0.3\%$ SE	93.55	94.87	97.10	0.4040	0.4034	0.3480	– 0.1436	0.5396	0.3742
galactose	H_2O	109.64	110.00	111.31	0.3935	0.3808	0.3807	0.0879	0.0777	0.0857
	$H_2O + 0.1\%$ SE	110.12	110.84	111.53	0.4042	0.3862	0.3340	0.0521	0.0934	0.1145
	$H_2O + 0.3\%$ SE	110.80	111.22	111.66	0.4229	0.4127	0.3681	0.0961	0.1033	0.1064
fructose	H_2O	113.53	114.66	116.50	0.4370	0.4210	0.4197	– 0.0111	0.0415	0.0294
	$H_2O + 0.1\%$ SE	114.27	115.20	117.01	0.4665	0.4011	0.3600	– 0.0318	0.0381	0.0637
	$H_2O + 0.3\%$ SE	114.84	115.76	117.43	0.4460	0.4018	0.3700	– 0.0376	– 0.0690	0.0180
glucose	H_2O	116.87	117.26	118.79	0.4428	0.3959	0.4111	0.0704	0.0629	0.0727
	$H_2O + 0.1\%$ SE	117.34	117.65	119.14	0.4317	0.3449	0.3556	0.0663	0.0573	0.0892
	$H_2O + 0.3\%$ SE	117.88	118.07	119.81	0.4575	0.3713	0.4781	0.0822	0.0606	0.0326
sucrose	H_2O	211.55	212.13	214.12	0.7850	0.7747	0.7511	0.5272	0.4578	0.4036
	$H_2O + 0.1\%$ SE	211.96	212.29	214.38	0.7897	0.7477	0.7100	0.5392	0.5188	0.4541
	$H_2O + 0.3\%$ SE	213.25	213.85	215.34	0.8120	0.7506	0.7020	0.5204	0.5395	0.4885
lactose	H_2O	224.18	225.31	227.72	0.8356	0.8010	0.8004	0.5418	0.5472	0.4556
	$H_2O + 0.1\%$ SE	224.57	225.84	228.21	0.8787	0.8445	0.8082	0.5437	0.4952	0.4982
	$H_2O + 0.3\%$ SE	224.90	226.43	228.98	0.9415	0.8989	0.8657	0.4012	0.3886	0.3395
maltose	H_2O	227.69	227.86	229.81	0.9022	0.8340	0.8215	0.4767	0.5922	0.4955
	$H_2O + 0.1\%$ SE	227.98	228.16	230.26	0.9817	0.8596	0.7654	0.2783	0.3969	0.4604
	$H_2O + 0.3\%$ SE	228.05	228.68	230.86	1.0113	0.9942	0.8101	0.2325	0.1342	0.4502

temperatures may cause the desolvation of micelles and their counterions providing thus an easier access for the additive into the more hydrophobic interior of the micelle. The results may also suggest that carbohydrate molecules prefer to be in a micellar-like environment where there is less free space than in the carbohydrate in water environment.

The order of limiting apparent molar volumes (ϕ_v°) obtained for the carbohydrates in water and in water-Surf Excel solutions are (Table 2):

(i) Monosaccharides: $L(+)$-arabinose < $D(+)$-galactose < $D(-)$-fructose < $D(+)$-glucose;
(ii) Disaccharides: sucrose < lactose < maltose.

The order of the monosaccharides may be due to the fact that $L(+)$-arabinose has less OH groups and carbon atoms in the chain than $D(+)$-galactose, suggesting that galactose is comparatively more hydrated than arabinose. The ϕ_v° values for glucose at all temperatures are higher than those of galactose and fructose. The higher ϕ_v° values of glucose suggest that it is comparatively more hydrated than fructose and galactose. Glucose and galactose are present in form of pyranose with the difference that in galactose the OH group at the C-4 carbon atom is configurationally different from that in glucose. Galactose has a higher percentage of axial OH groups than glucose and probably for that reason exhibits a lower value of ϕ_v° as compared to glucose [14]. Slightly higher hydration in glucose over fructose can be ascribed to the six-membered pyranose ring in glucose being more favourable for interactions with water compared to the five membered furanose ring in fructose.

The stereospecific hydration observed in water and in water-SE solution systems for monosaccharides is also observed in solutions of disaccharides. The ϕ_v° values of maltose at all studied temperatures are higher than those of sucrose and lactose, although the difference is not very large. The higher ϕ_v° values in case of maltose suggest that it is comparatively more hydrated than sucrose and lactose. Maltose is made up of two glucose units whereas sucrose is made up of one molecule of glucose and one molecule of fructose and lactose consists of one molecule of galactose and one molecule of glucose. As mentioned earlier, galactose contains a higher percentage of axial OH groups than glucose. Since maltose contains two glucose units (higher percentage of equatorial OH) and both sucrose and lactose contain only one glucose unit, obviously maltose will exhibit higher values of ϕ_v° as compared to sucrose and lactose. The slightly higher ϕ_v° value in lactose over sucrose can be ascribed to the six-membered pyranose ring in lactose being more favourable for interactions with water and the water-SE system than the five membered furanose ring in sucrose.

The viscosities (η) of the sugars in water and in water – 0.1% and 0.3% SE solutions were measured at 308.15; 313.15 and 328.15 K respectively. The relevant data are shown in Table 3 and their representative plots are shown in Fig. 3, as example. From Fig. 3 it is seen that the viscosity *vs.* molality curves for all the systems are almost linear in nature in all the solvent systems. At constant temperature the value of η increases with the increase in molality of all the studied carbohydrates in all the solvent systems. As the temperature increases the corresponding viscosity decreases in all cases. It is also found that the values of η are higher in

Table 3. Viscosity (η/cP) for the carbohydrates in water, water – 0.1% SE, and water – 0.3% SE solutions at 308.15, 313.15, and 323.15 K

Molality (mol kg^{-1})	η at 308.15 K							η at 313.15 K							η at 323.15 K						
	arabinose	galactose	fructose	glucose	sucrose	lactose	maltose	arabinose	galactose	fructose	glucose	sucrose	lactose	maltose	arabinose	galactose	fructose	glucose	sucrose	lactose	maltose
In water solution																					
0.2000	0.7517	0.7782	0.7815	0.7895	0.8520	0.8565	0.8608	0.6783	0.6973	0.7094	0.7157	0.7734	0.7751	0.7784	0.5692	0.5819	0.5867	0.5924	0.6425	0.6439	0.6447
0.4000	0.7656	0.8226	0.8448	0.8569	1.0110	1.0225	1.0242	0.6879	0.7423	0.7595	0.7723	0.9016	0.9121	0.9243	0.5770	0.6176	0.6330	0.6397	0.7503	0.7523	0.7561
0.6000	0.7745	0.8731	0.9102	0.9358	1.1973	1.2173	1.2235	0.6947	0.7846	0.8179	0.8363	1.0635	1.0512	1.0898	0.5894	0.6488	0.6754	0.6920	0.8690	0.8736	0.8894
0.8000	0.7882	0.9289	0.9848	1.0143	1.4155	1.4326	1.4521	0.7078	0.8327	0.8831	0.9066	1.2496	1.2635	1.2889	0.5954	0.6905	0.7205	0.7469	1.0209	1.0308	1.0438
1.0000	0.8048	0.9878	1.0544	1.1020	1.6779	1.7012	1.7263	0.7249	0.8862	0.9474	0.9825	1.4786	1.5019	1.5206	0.6036	0.7244	0.7746	0.8051	1.1928	1.2141	1.2253
In water + 0.1% SE solution																					
0.2000	0.7547	0.7860	0.7900	0.8016	0.8616	0.8632	0.8651	0.6787	0.7042	0.7178	0.7183	0.7750	0.7798	0.7838	0.5658	0.5862	0.5930	0.5939	0.6429	0.6431	0.6434
0.4000	0.7663	0.8297	0.8486	0.8619	1.0142	1.0295	1.0455	0.6918	0.7451	0.7626	0.7783	0.9097	0.9186	0.9390	0.5769	0.6181	0.6332	0.6432	0.7507	0.7589	0.7685
0.6000	0.7747	0.8875	0.9199	0.9364	1.2072	1.2486	1.2955	0.7019	0.7904	0.8258	0.8392	1.0985	1.1128	1.1379	0.5852	0.6601	0.6808	0.6940	0.8699	0.8856	0.9123
0.8000	0.7963	0.9464	0.9941	1.0190	1.4301	1.4562	1.4801	0.7146	0.8500	0.8899	0.9153	1.2678	1.2851	1.3098	0.5964	0.7011	0.7333	0.7495	1.0246	1.0422	1.0625
1.0000	0.8125	0.9892	1.0681	1.1066	1.7095	1.7271	1.7399	0.7348	0.8849	0.9571	0.9932	1.5005	1.5226	1.5407	0.6089	0.7356	0.7868	0.8111	1.1982	1.2098	1.2249
In water + 0.3% SE solution																					
0.2000	0.7645	0.7992	0.7998	0.8064	0.8797	0.8829	0.8954	0.6836	0.7213	0.7219	0.7226	0.7830	0.7927	0.8031	0.5797	0.6003	0.6111	0.6120	0.6545	0.6599	0.6686
0.4000	0.7772	0.8424	0.8632	0.8726	1.0261	1.0387	1.0550	0.7002	0.7655	0.7755	0.7845	0.9172	0.9268	0.9366	0.5889	0.6374	0.6472	0.6563	0.7610	0.7696	0.7765
0.6000	0.7899	0.8897	0.9302	0.9474	1.2275	1.2401	1.2509	0.7122	0.7986	0.8326	0.8492	1.0938	1.1015	1.1106	0.6013	0.6679	0.6942	0.7116	0.8955	0.9026	0.9132
0.8000	0.8066	0.9596	1.0083	1.0305	1.4674	1.4729	1.4826	0.7205	0.8491	0.8978	0.9213	1.3058	1.3062	1.3081	0.6065	0.7166	0.7476	0.7635	1.0564	1.0652	1.0717
1.0000	0.8201	1.0051	1.0871	1.1264	1.7342	1.7391	1.7469	0.7319	0.9032	0.9651	0.9977	1.5239	1.5326	1.5423	0.6125	0.7507	0.7989	0.8289	1.2307	1.2390	1.2440

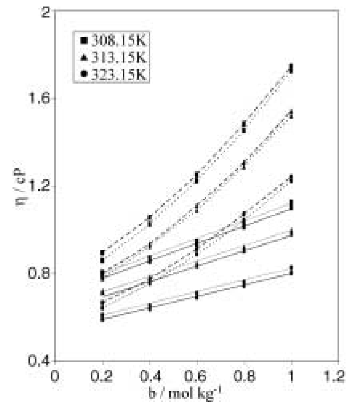

Fig. 3. Plots of viscosity (η) versus molality for (a) glucose (solid line) and maltose (dashed line) in water; (b) glucose (dotted line) and maltose (long dashed line) in water – 0.3% SE solutions at 308.15, 313.15, and 323.15 K

water-SE solvent systems than in the pure water system. This suggests that carbohydrate molecules prefer to be in a micellar-like environment where there is relatively less free space than in the water environment. The viscosities of all the carbohydrates are found to increase at a particular temperature in water and also in water-SE solutions in the order (Table 3):

(i) Monosaccharides: *L*(+)-Arabinose < *D*(+)-galactose < *D*(−)-fructose < *D*(+)-glucose;
(ii) Disaccharides: sucrose < lactose < maltose.

From this it is evident that the viscosity of the carbohydrate molecules in solutions depend on the molecular weight, structural formula and the orientation of the OH groups in the carbohydrate. This behaviour indicates that the structure of water existing in pure is affected by the carbohydrate molecules as well as by the surfactant molecules. Each carbohydrate molecule contains several higher polar OH groups which appear to be highly associated with the solvent due to strong intermolecular interactions (hydrogen bonding) and dipole–dipole interactions. The η values of glucose are higher than those for the remaining monosaccharides. Similarly maltose showed a higher η value than the remaining disaccharide molecules studied. This may be accounted for the presence of a higher percentage of equatorial OH groups in the glucose unit as mentioned earlier. These observations from viscosity data are in excellent agreement with those obtained from volumetric data for all monosaccharides and disaccharides. According to the 'flickering cluster' model of water [15] there are larger voids within the hydrogen-bonded framework of water. Carbohydrate molecules which form hydrogen bonded species appear to have a positive interaction with water. These interactions seem to be strong as is evident from the viscosity *vs.* molality curves. Thus the carbohydrate molecules can be classified as water structure maker. This is clearly supported by the nature of the viscosity *B*-coefficient data. The values of *B*-coefficients usually reflect solute–solvent interactions [16]. A positive value of the *B*-coefficient corresponds to the structure making properties of the solute. On the other hand, a

Table 4. Free energy of activation ($\Delta G^{\neq}$/kJ mol^{-1}) for the carbohydrates in water, water – 0.1% SE, and water – 0.3% SE solutions at 308.15, 313.15, and 323.15 K

Molality (mol kg^{-1})	$\Delta G^{\neq}$ at 308.15 K							$\Delta G^{\neq}$ at 313.15 K							$\Delta G^{\neq}$ at 323.15 K						
	arabinose	galactose	fructose	glucose	sucrose	lactose	maltose	arabinose	galactose	fructose	glucose	sucrose	lactose	maltose	arabinose	galactose	fructose	glucose	sucrose	lactose	maltose
In water solution																					
0.2000	9.00	9.18	9.19	9.21	9.22	9.46	9.49	8.90	9.05	9.07	9.11	9.11	9.36	9.39	8.71	8.87	8.88	8.91	8.93	9.18	9.19
0.4000	9.06	9.38	9.44	9.47	9.51	9.99	10.04	8.94	9.27	9.35	9.36	9.40	9.86	9.94	8.76	9.08	9.14	9.16	9.21	9.69	9.73
0.6000	9.13	9.59	9.68	9.74	9.78	10.51	10.59	8.99	9.47	9.56	9.61	9.67	10.38	10.47	8.83	9.27	9.36	9.42	9.47	10.18	10.27
0.8000	9.16	9.80	9.93	9.99	10.08	11.03	11.12	9.03	9.67	9.81	9.86	9.95	10.89	11.00	8.87	9.49	9.59	9.67	9.78	10.70	10.79
1.0000	9.21	10.00	10.15	10.24	10.35	11.55	11.65	9.08	9.89	10.04	10.12	10.24	11.41	11.52	8.91	9.67	9.83	9.92	10.04	11.21	11.32
In water + 0.1% SE solution																					
0.2000	9.02	9.21	9.22	9.25	9.26	9.48	9.60	8.90	9.08	9.12	9.12	9.14	9.37	9.41	8.71	8.88	8.91	8.92	8.94	9.18	9.19
0.4000	9.07	9.40	9.45	9.48	9.52	10.00	10.09	8.94	9.28	9.33	9.37	9.42	9.88	9.98	8.75	9.08	9.14	9.17	9.21	9.69	9.77
0.6000	9.12	9.63	9.70	9.74	9.80	10.53	10.74	9.00	9.49	9.59	9.62	9.68	10.46	10.58	8.81	9.32	9.38	9.42	9.49	10.18	10.33
0.8000	9.17	9.84	9.95	10.00	10.08	11.05	11.17	9.05	9.73	9.83	9.89	9.95	10.92	11.04	8.86	9.53	9.63	9.68	9.76	10.71	10.84
1.0000	9.23	10.01	10.18	10.25	10.36	11.59	11.67	9.11	9.88	10.06	10.14	10.23	11.44	11.55	8.92	9.71	9.87	9.93	10.03	11.22	11.32
In water + 0.3% SE solution																					
0.2000	9.06	9.25	9.24	9.26	9.31	9.54	9.59	8.92	9.14	9.13	9.15	9.19	9.39	9.47	8.76	9.06	8.99	8.96	8.99	9.22	9.29
0.4000	9.10	9.44	9.49	9.51	9.52	10.02	10.11	8.96	9.35	9.37	9.39	9.44	9.90	9.97	8.81	9.23	9.20	9.23	9.27	9.73	9.80
0.6000	9.15	9.63	9.73	9.77	9.83	10.57	10.64	9.03	9.51	9.60	9.64	9.72	10.45	10.51	8.87	9.42	9.43	9.49	9.54	10.26	10.31
0.8000	9.20	9.87	9.98	10.03	10.16	11.11	11.17	9.06	9.72	9.85	9.90	10.02	11.00	11.03	8.93	9.69	9.68	9.73	9.83	10.79	10.86
1.0000	9.26	10.04	10.22	10.30	10.40	11.63	11.68	9.13	9.93	10.08	10.15	10.26	11.48	11.55	8.97	9.88	9.91	9.99	10.08	11.29	11.31

negative value of the *B*-coefficient indicates the structure breaking behaviour of the solute [17]. The *B* values of the sugars in water and also in water-SE solutions are presented in Table 3 at 308.15, 313.15 and 323.15 K. Positive *B* values have been found in all cases. This is a clear indication of the structure making property of all the carbohydrate molecules in both the solvent systems. The *B*-coefficient values of glucose are higher than those of the remaining studied monosaccharides. Similarly, maltose has higher *B*-coefficient values than those of the remaining disaccharides. It is also observed from Table 3 that the value of the *B*-coefficient depends on temperature. Most of the *B*-coefficient values decrease with the rise of temperature. This is probably due to greater thermal agitation and reduction of attractive forces between solute–solvent systems [18]. Increase of some of the *B*-coefficient values with the rise of temperature may be due to the inter-penetration effect which brings the molecules closer together. The increase of *B*-coefficients of carbohydrates with the increase of Surf-Excel molality reveals that these carbohydrates gain progressively a more structured environment as Surf-Excel molality is increased. In ternary (H_2O + Surf-Excel + carbohydrates) solution, Surf-Excel polar group interactions disrupt the less structured region around them and the water molecules move to the more structured bulk region, resulting in an increase in viscosity *B*-coefficients. The Surf Excel-carbohydrates and Surf-Excel – Surf-Excel interactions progressively enhance the overall micellar structure of the solution as the molality of SE is increased reflecting the increase in *B*-coefficient values.

The *D*-coefficient value represents the solute–solute interactions coupled with the size and shape effect of the solute and to some extent the solute–solvent interactions. Due to the lack of adequate theoretical knowledge, its significance is not fully understood [13]. In the present study no regularity in *D*-coefficient values were found in most of the systems. Except *L*(+)-arabinose and *D*(−)-fructose all the values of *D*-coefficients are positive. These positive *D* values may represent the increase in viscosity with solute concentration due to some additional factors other than the solute–solvent interactions (*B*-coefficient). The negative value of the *D*-coefficient indicates that the increase in viscosity with the solute concentration may be due to some eliminating factors other than the solute–solvent interactions which imparts negative contribution to the increase in viscosity.

It can be seen from Table 4 that the free energy of activation ($\Delta G^{\neq}$) is positive for the viscous flow of all investigated sugars in all concentration for all the solvent systems at all temperatures. $\Delta G^{\neq}$ increases with the increase in solute concentration and decreases with the rise of temperature. This behaviour of $\Delta G^{\neq}$ suggests that positive work is required to create holes for viscous flow and to weaken the solute–solvent and solvent–solvent interactions at higher temperature due to thermal agitation. The positive value of $\Delta H^{\neq}$ increases with the increase of solute composition (data not shown). This indicates that to overcome the energy barrier more positive work has to be done. Thus the viscous flow is not favoured for all the carbohydrate molecules in solution systems. This may be due to the fact that the ground state of the binary and ternary systems is more organized than the transition states. The systems have to traverse these transition states during the viscous flow.

Conclusion

Apparent molar volume and viscosity data on carbohydrate molecules in water and in water-SE solution systems reveal the following:

1. The molecules *L*(+)-arabinose, *D*(+)-galactose, *D*(−)-fructose, and *D*(+)-glucose exhibit structure making behaviour in water and in water-SE solution systems. Arabinose is less hydrated compared to the other monosaccharides studied.
2. The disaccharides sucrose, lactose, and maltose exhibit structure making behaviour in water and in water-SE solutions. Maltose is more hydrated than sucrose and lactose probably due to its higher percentage of equatorial OH.
3. Carbohydrate molecules in water-SE systems are likely to be in a micellar like environment where there is relatively less free space than in the water environment. At a fixed SE concentration and temperature, increasing the concentration of added carbohydrate results in an increase in micellar size and weight.
4. The viscous flow of carbohydrate molecules in solutions is not favored. As the concentration of SE increases the ground state becomes more organized, as a result the net work necessary to traverse the transition state during viscous flow increases.

Experimental

L(+)-Arabinose (99%), *D*(+)-galactose (> 98%), *D*(−)-fructose (99%), *D*(+)-glucose (> 99%), were procured from E. Merck. Sucrose (99%), maltose (> 98%), lactose (99%) were purchased from BDH. Surf-Excel, a commercial detergent power (India) was procured from a local market at Rajshahi, Bangladesh. The chemicals with quoted purities were dried first in an oven at 110°C and then at room temperature in vacuum over phosphorus pentoxide for at least 24 h and were then used without further purification. Doubly distilled water was used for making up solutions and densities were measured by using a 5 ml bicapillary pycnometer previously calibrated with water. Viscosity was measured by means of a calibrated U-type *Ostwald* viscometer of the British standard institution with sufficiently long efflux time to avoid kinetic energy correction. Time of flow was recorded by a timer accurate up to ± 0.01 s. A Mettler PM-200 electronic balance with an accuracy of ± 0.0001 g was used for weighing. Temperatures were controlled within ± 0.1°C by a thermostatic water bath.

Acknowledgement

We acknowledge the Department of Chemistry, University of Rajshahi for providing laboratory and other relevant facilities for the work.

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