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Thermodynamic and Transport Properties of Some Disaccharides in Aqueous Ammonium Sulfate Solutions at Various Temperatures

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Apparent molar volumes, $V_{2,\phi}$, and viscosities, η, of disaccharides D-(+)-maltose monohydrate, D-(+)-lactose monohydrate, sucrose, and D-(+)-cellobiose in water and in (0.49850 and 0.99705) mol·kg^{-1} aqueous solutions of ammonium sulfate $\{(NH_4)_2SO_4\}$ have been determined from density, ρ, and efflux time, t, measurements, respectively, at temperatures (288.15, 298.15, 308.15, and 318.15) K. The refractive indices, n_D, for these systems have also been determined. From these data, the standard partial molar volumes, V_2^{∞}, at infinite dilution and viscosity B-coefficients (using the Jones−Dole equation) have been determined at different temperatures. The standard partial molar volumes of transfer, $\Delta_t V_2^{\infty}$, and B-coefficients of transfer, $\Delta_t B$, have been estimated for the transfer of disaccharides from water to aqueous ammonium sulfate solutions. Partial molar expansion coefficients, $(\partial V_2^{\infty}/\partial T)_P$ and $(\partial^2 V_2^{\infty}/\partial T^2)_P$, and dB/dT coefficients have also been estimated. Gibbs free energy of activation of viscous flow has been calculated by using Feakin's transition-state theory for the studied systems. The various parameters have been utilized to rationalize the hydration behavior of disaccharides.

Introduction

Saccharides are widely distributed in various forms of life as essential moieties of glycoproteins, glycolipids, nucleic acids, and polysaccharides. Their solution properties are of considerable interest for various aspects of basic research and in many applications as well.[1–3] It has been demonstrated that saccharides, and in particular disaccharides (trehalose and sucrose), can stabilize labile biomolecules in aqueous solutions by a combination of kinetic and specific effects.[4]

The presence of salts modifies important properties of aqueous saccharide solutions related to their protective role, such as viscosity, water sorption, crystallization rate, and glass transition temperature.[5] The hydration characteristics of saccharides in aqueous solutions are a key feature in determining their structural and functional properties and to understanding the mechanisms of various biological processes like protein stability, antidesiccation,[6–9] etc.

Thermodynamic and transport properties are very useful in the study of hydration behavior of saccharides. We have studied mono-, di-, and trisaccharides in a variety of electrolytic media and alkylammonium salts.[10–14] Recently, we have reported[10] the hydration behavior of some disaccharides (D-(+)-cellobiose, D-(+)-lactose monohydrate, D-(+)-maltose monohydrate, and sucrose) in the presence of aqueous solutions of sodium sulfate, as it is a stronger structure-maker having a salting-in effect on the peptide group and a strong salting-out effect on the hydrophobic group. Sodium sulfate also stabilizes the native structure of proteins.[15] It has been reported[16] that ammonium sulfate has a strong ability to salt-out proteins, and this salting-out effect increases with salt concentration. Therefore, it will be interesting to study and compare the behavior of disaccharides in the presence of aqueous solutions of these two salts. In continuation of our work on saccharides,[10–14] we report herein the apparent molar volumes, V_{ϕ}, viscosities, η, and refractive indices, n_D, for disaccharides viz., D-(+)-maltose monohydrate, D-(+)-lactose monohydrate, sucrose, and D-(+)-cellobiose in (0.49850 and 0.99705) mol·kg^{-1} aqueous solutions of ammonium sulfate $\{(NH_4)_2SO_4\}$ at (288.15, 298.15, 308.15, and 318.15) K. Standard partial molar volumes of transfer, $\Delta_t V_2^{\infty}$, at infinite dilution and viscosity B-coefficients of transfer, $\Delta_t B$, from water to aqueous solutions of $(NH_4)_2SO_4$ (cosolute) have also been determined. The Gibbs free energies of activation, $\Delta\mu_2^{\infty\ddagger}$, for viscous flow of disaccharides have been determined by applying the transition-state theory. The signs and magnitude of transfer parameters have been interpreted in terms of various interactions occurring in these solutions.

Experimental Section

D-(+)-Lactose monohydrate, D-(+)-maltose monohydrate, D-(+)-cellobiose (AR, Sisco Research Laboratories, India), and sucrose (Lancaster, 99 %) were used as received without further purification; however, these chemicals were dried over P_2O_5 in a vacuum desiccator for 48 h before use. All the solutions were prepared in doubly distilled−deionized and degassed water. The solutions were prepared by mass with a Sartorius balance with a precision of ± 0.01 mg.

A vibrating-tube digital densimeter (model DMA 60/602, Anton Paar, Austria) was used to measure the densities of the solutions. An efficient constant-temperature bath (Heto Birkerod/Denmark), with a stability within ± 0.01 K, was used to control the temperature of the water circulating around the densimeter cell. The reproducibility in the density measurements was ± $3 \cdot 10^{-6}$ g·cm^{-3} on average. The functioning of the densimeter was checked by determining densities of aqueous sodium

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Table 1. Densities, ρ, and Apparent Molar Volumes, $V_{2,\phi}$, for Some Disaccharides in Water and in Aqueous Ammonium Sulfate Solutions as a Function of the Molalities of Disaccharides and Ammonium Sulfate at Different Temperatures

m / mol·kg^{-1}	$\rho\cdot10^{-3}$ / kg·m^{-3}	$V_{2,\phi}\cdot10^{6}$ / $\text{m}^3\text{·mol}^{-1}$	m / mol·kg^{-1}	$\rho\cdot10^{-3}$ / kg·m^{-3}	$V_{2,\phi}\cdot10^{6}$ / $\text{m}^3\text{·mol}^{-1}$
D-(+)-Maltose Monohydrate					
$m_B/\text{mol·kg}^{-1} = 0.49850$ [a]					
at 288.15 K			$\rho_o\cdot10^{-3}/\text{kg·m}^{-3} = 1.039149$[b]		
0.04928	1.045257	230.58	0.53310	1.098301	230.77
0.06950	1.047721	230.59	0.82350	1.125095	230.88
0.10055	1.051454	230.61	1.23154	1.157885	231.05
at 298.15 K			$\rho_o\cdot10^{-3}/\text{kg·m}^{-3} = 1.037150$		
0.04928	1.043110	233.61	0.53310	1.094806	233.84
0.06950	1.045509	233.62	0.82350	1.120857	234.08
0.10055	1.049152	233.63	1.23154	1.152573	234.18
at 308.15 K			$\rho_o\cdot10^{-3}/\text{kg·m}^{-3} = 1.033063$		
0.04928	1.038881	236.74	0.53310	1.089744	237.01
0.06950	1.041218	236.75	0.82350	1.114651	237.21
0.10055	1.044869	236.76	1.23154	1.145425	237.46
at 318.15 K			$\rho_o\cdot10^{-3}/\text{kg·m}^{-3} = 1.027668$		
0.04928	1.033243	242.17	0.53310	1.081459	242.35
0.06950	1.035490	242.18	0.82350	1.105688	242.47
0.10055	1.038893	242.20	1.23154	1.135104	242.64
$m_B/\text{mol·kg}^{-1} = 0.99705$					
at 288.15 K			$\rho_o\cdot10^{-3}/\text{kg·m}^{-3} = 1.071086$		
0.05164	1.077065	234.15	0.10065	1.082582	234.30
0.07194	1.079370	234.21	0.14717	1.087691	234.41
0.08340	1.080657	234.24			
at 298.15 K			$\rho_o\cdot10^{-3}/\text{kg·m}^{-3} = 1.065091$		
0.05164	1.070867	238.41	0.10065	1.076202	238.49
0.07194	1.073096	238.44	0.14717	1.081144	238.54
0.08340	1.074340	238.46			
at 308.15 K			$\rho_o\cdot10^{-3}/\text{kg·m}^{-3} = 1.057658$		
0.05164	1.063147	244.35	0.10065	1.068215	244.46
0.07194	1.065265	244.39	0.14717	1.072905	244.53
0.08340	1.066447	244.43			
at 318.15 K			$\rho_o\cdot10^{-3}/\text{kg·m}^{-3} = 1.047031$		
0.05164	1.051717	260.17	0.10065	1.056037	260.27
0.07194	1.053522	260.21	0.14717	1.060026	260.35
0.08340	1.054530	260.23			
D-(+)-Lactose Monohydrate					
$m_B/\text{mol·kg}^{-1} = 0.49850$					
at 288.15 K					
0.04902	1.045300	229.19	0.11992	1.053927	229.35
0.06891	1.047751	229.24	0.15050	1.057544	229.45
0.08902	1.050204	229.29	0.20280	1.063634	229.55
at 298.15 K					
0.04902	1.043177	231.75	0.11992	1.051625	231.93
0.06891	1.045577	231.81	0.15050	1.055173	232.00
0.08902	1.047979	231.87	0.20280	1.061128	232.13
at 308.15 K					
0.04902	1.038967	234.56	0.11992	1.047237	234.76
0.06891	1.041319	234.61	0.15050	1.050711	234.83
0.08902	1.043669	234.67	0.20280	1.056541	234.96
at 318.15 K					
0.04902	1.033354	239.37	0.11992	1.041306	239.64
0.06891	1.035616	239.44	0.15050	1.044641	239.75
0.08902	1.037879	239.54	0.20280	1.050250	239.92
$m_B/\text{mol·kg}^{-1} = 0.99705$					
at 288.15 K					
0.05009	1.076982	232.52	0.09984	1.082685	232.61
0.06747	1.078993	232.55	0.14470	1.087701	232.69
0.09286	1.081895	232.59			
at 298.15 K					
0.05009	1.070778	236.94	0.09984	1.076270	237.08
0.06747	1.072715	237.00	0.14470	1.081100	237.19
0.09286	1.075508	237.06			
at 308.15 K					
0.05009	1.063170	241.03	0.09984	1.068493	241.18
0.06747	1.065048	241.07	0.14470	1.073173	241.27
0.09286	1.067755	241.15			
at 318.15 K					
0.05009	1.052144	249.82	0.09984	1.057080	249.90
0.06747	1.053884	249.84	0.14470	1.061423	249.96

Table 1 Continued

$\frac{m}{\mathrm{mol \cdot kg^{-1}}}$	$\frac{\rho \cdot 10^{-3}}{\mathrm{kg \cdot m^{-3}}}$	$\frac{V_{2,\phi} \cdot 10^{6}}{\mathrm{m^{3} \cdot mol^{-1}}}$	$\frac{m}{\mathrm{mol \cdot kg^{-1}}}$	$\frac{\rho \cdot 10^{-3}}{\mathrm{kg \cdot m^{-3}}}$	$\frac{V_{2,\phi} \cdot 10^{6}}{\mathrm{m^{3} \cdot mol^{-1}}}$
0.09286	1.056398	249.88			
		Sucrose			
		m_B/mol·kg^{-1} = 0.49850			
at 288.15 K					
0.04864	1.045221	212.56	0.14957	1.057333	213.04
0.06994	1.047828	212.65	0.20226	1.063436	213.23
0.10231	1.051743	212.82			
at 298.15 K					
0.04864	1.043152	214.05	0.14957	1.055158	214.39
0.06994	1.045734	214.12	0.20226	1.061188	214.58
0.10231	1.049610	214.24			
at 308.15 K					
0.04864	1.038907	217.54	0.14957	1.050589	217.84
0.06994	1.041420	217.60	0.20226	1.056478	217.94
0.10231	1.045190	217.71			
at 318.15 K					
0.04864	1.033310	222.03	0.14957	1.044575	222.39
0.06994	1.035737	222.11	0.20226	1.050243	222.51
0.10231	1.039357	222.21			
		m_B/mol·kg^{-1} = 0.99705			
at 288.15 K					
0.04863	1.076924	213.78	0.15080	1.088728	214.08
0.06687	1.079075	213.85	0.20054	1.094273	214.16
0.09835	1.082740	213.95			
at 298.15 K					
0.04863	1.070863	215.57	0.15080	1.082539	215.82
0.06687	1.072991	215.62	0.20054	1.088025	215.92
0.09835	1.076620	215.69			
at 308.15 K					
0.04863	1.063078	222.86	0.15080	1.074022	223.17
0.06687	1.065075	222.92	0.20054	1.079158	223.26
0.09835	1.068473	223.02			
at 318.15 K					
0.04863	1.052185	229.10	0.15080	1.062575	229.46
0.06687	1.054082	229.16	0.20054	1.067428	229.67
0.09835	1.057312	229.27			
		D-(+)-Cellobiose			
		m_B/mol·kg^{-1} = 0.49850			
at 288.15 K					
0.04897	1.045781	202.67	0.09044	1.051251	203.12
0.06963	1.048518	202.92	0.15175	1.059080	203.86
at 298.15 K					
0.04897	1.043578	206.72	0.09044	1.048896	206.97
0.06963	1.046239	206.88	0.15175	1.056513	207.54
at 308.15 K					
0.04897	1.039262	211.46	0.09044	1.044396	211.59
0.06963	1.041833	211.53	0.15175	1.051807	211.76
at 318.15 K					
0.04897	1.033629	216.59	0.09044	1.038563	216.75
0.06963	1.036099	216.67	0.15175	1.045669	216.96
		m_B/mol·kg^{-1} = 0.99705			
at 288.15 K					
0.04368	1.076839	203.64	0.08750	1.082490	203.75
0.06755	1.079933	203.70	0.14525	1.089760	203.90
at 298.15 K					
0.04368	1.070633	208.43	0.08750	1.076071	208.59
0.06755	1.073612	208.52	0.14525	1.083067	208.76
at 308.15 K					
0.04368	1.063050	212.19	0.08750	1.068341	212.35
0.06755	1.065945	212.28	0.14525	1.075136	212.56
at 318.15 K					
0.04368	1.051944	223.29	0.08750	1.056762	223.40
0.06755	1.054581	223.36	0.14525	1.062949	223.56

[a] m_B = molality of ammonium sulfate in water. [b] ρ_o = density of ammonium sulfate in water.

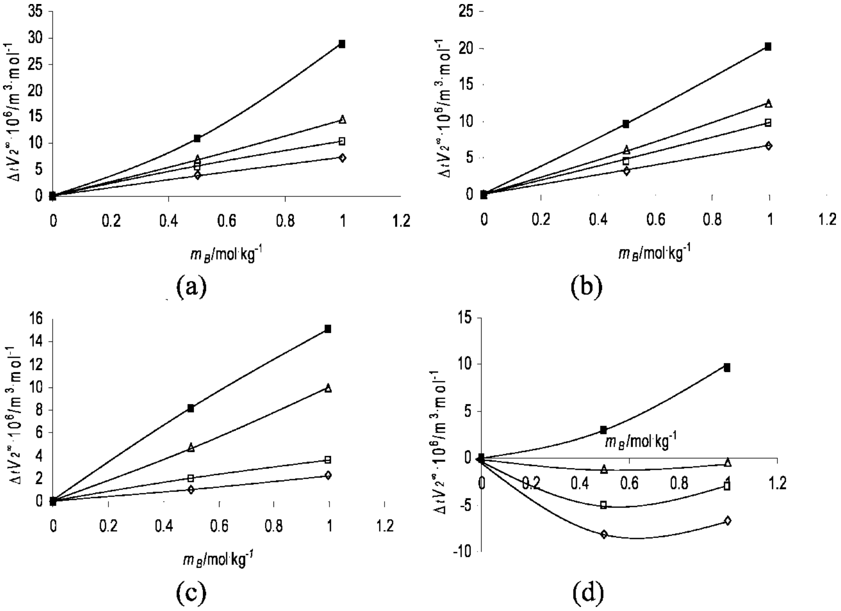
chloride solutions, which agreed very well with the literature[17] values.

An Ubbelohde-type capillary viscometer was calibrated by measuring the efflux time of water from (298.15 to 318.15) K using viscosity and density data from the literature.[10] The efflux time was measured with a digital stopwatch with a resolution of ± 0.01 s for the average of at least four flow time readings. The temperature of the thermostat was controlled to within ±

Table 2. Standard Partial Molar Volumes, V_2^∞, at Infinite Dilution for Some Disaccharides in Water and in Aqueous Ammonium Sulfate Solutions at Different Temperatures

	$V^\infty_{2,\phi}\cdot 10^6/\mathrm{m^3\cdot mol^{-1}}$ at various m_B/mol·kg^{-1a}		
disaccharides	^{b}water	0.49850	0.99705
at 288.15 K			
D-(+)-maltose monohydrate	226.60 ± ^{c}0.03 ^{d}(3.55)	230.56 ± 0.01 (0.39)	234.01 ± 0.01 (2.73)
D-(+)-lactose monohydrate	225.74 ± 0.01 (1.74)	229.08 ± 0.01 (2.37)	232.43 ± 0.01 (1.80)
sucrose	211.34 ± 0.02 (1.02)	212.35 ± 0.02 (4.44)	213.68 ± 0.03 (2.49)
D-(+)-cellobiose	210.21 ± 0.02 (8.50)	202.10 ± 0.02 (11.54)	203.53 ± 0.01 (2.56)
at 298.15 K			
D-(+)-maltose monohydrate	228.14 ± 0.01 (1.56) ^{e}210.00 ± 0.01 (1.87) ^{f}228.14 ± 0.07 ^{g}210.07	233.58 ± 0.04 (0.51)	238.34 ± 0.01 (1.37) ^{e}220.43 ± 0.01 (1.50)
D-(+)-lactose monohydrate	227.03 ± 0.01 (0.77) ^{e}208.94 ± 0.01 (0.85) ^{f}227.03 ± 0.04 ^{g}208.96	231.64 ± 0.01 (2.41)	236.82 ± 0.01 (2.60) ^{e}218.89 ± 0.02 (3.10)
sucrose	211.92 ± 0.02 (1.25) ^{f}211.92 ± 0.08	213.88 ± 0.01 (3.44)	215.46 ± 0.01 (2.31)
D-(+)-cellobiose	211.31 ± 0.02 (8.00) ^{f}211.31 ± 0.04	206.31 ± 0.05 (7.99)	208.30 ± 0.01 (3.21)
at 308.15 K			
D-(+)-maltose monohydrate	229.70 ± 0.02 (3.34) ^{f}229.72 ± 0.03 ^{g}211.61	236.70 ± 0.01 (0.61)	244.26 ± 0.01 (1.88)
D-(+)-lactose monohydrate	228.36 ± 0.02 (2.69) ^{f}228.36 ± 0.02	234.43 ± 0.01 (2.62)	240.90 ± 0.01 (2.60)
sucrose	212.72 ± 0.02 (1.78) ^{f}212.74 ± 0.04	217.42 ± 0.02 (2.65)	222.72 ± 0.02 (2.67)
D-(+)-cellobiose	212.42 ± 0.01 (2.80) 212.42 ± 0.04	211.32 ± 0.01 (2.88)	212.03 ± 0.01 (3.63)
at 318.15 K			
D-(+)-maltose monohydrate	231.30 ± 0.01 (1.47) ^{f}231.30 ± 0.01	242.15 ± 0.01 (0.39)	260.07 ± 0.01 (1.89)
D-(+)-lactose monohydrate	229.60 ± 0.01 (2.33) ^{f}229.61 ± 0.01	239.19 ± 0.01 (3.58)	249.73 ± 0.01 (1.52)
sucrose	213.80 ± 0.02 (1.28) ^{f}213.81 ± 0.02	221.88 ± 0.02 (3.18)	228.90 ± 0.01 (3.74)
D-(+)-cellobiose	213.54 ± 0.02 (6.69) ^{f}213.54 ± 0.01	216.42 ± 0.01 (3.58)	223.18 ± 0.01 (2.63)

[a] m_B = molality of ammonium sulfate in water. [b] Ref 10. [c] Standard deviation. [d] slope = S_v/cm^3·kg·mol^{-2}. [e] The values for anhydrous samples obtained from those of the hydrated salts by applying molality correction to the data from ref 10. [f] Ref 14 (for hydrated). [g] Ref 14 (for anhydrous).



(a) (b)

(c) (d)

Figure 1. Standard partial molar volumes of transfer, $\Delta_t V_2^\infty$ of disaccharides (a) D-(+)-maltose monohydrate, (b) D-(+)- lactose monohydrate, (c) sucrose, and (d) D-(+)-cellobiose versus molalities, m_B, of $(NH_4)_2SO_4$ at ◇, 288.15 K; □, 298.15 K; Δ, 308.15 K; ■, 318.15 K.

0.01 K. The viscosities, η, of solutions were calculated by the following relation:

$$\eta/\rho = at - b/t \tag{1}$$

where ρ is the density of the solution; t is the efflux time; and a and b are the viscometric constants. The reproducibility of the measured viscosities was better than ± 0.001 mPa·s.

The refractive indices were measured with an Abbe refractometer with an error less than ± 0.001 units. The calibration was carried out with deionized, doubly distilled water. The temperature was maintained constant (within ± 0.01 K) by circulating water through the prism of the Abbe refractometer.

Results and Discussion

Apparent molar volumes, $V_{2,\phi}$, of D-(+)-maltose monohydrate, D-(+)-lactose monohydrate, sucrose, and D-(+)-cellobiose in 0.49850 and 0.99705 m_B (molality of cosolute in mol·kg^{-1}) aqueous solutions of $(NH_4)_2SO_4$ at (288.15, 298.15, 308.15, and 318.15) K were determined from the experimentally measured densities using the following relation

$$V_{2,\phi} = [M/\rho] - [(\rho - \rho_o)/(m\rho\rho_o)] \tag{2}$$

where M is the molar mass of the solute (disaccharide); m is the molality of the solution; and ρ_o and ρ are the densities of solvent and solution, respectively. Density and $V_{2,\phi}$ results for disaccharides in ammonium sulfate solutions are presented in Table 1 as a function of concentration and temperature (data for disaccharides in water have been reported[10,14] earlier). The uncertainty in the determined $V_{2,\phi}$ values resulting from the experimental uncertainties ranges from (0.09 to 0.02)·10^6 m^3·mol^{-1} for the lower (<0.05 mol·kg^{-1}) and higher concen

Table 3. Relative Viscosities, η_r, for Disaccharides in Water and in Aqueous Ammonium Sulfate Solutions at Different Temperatures

C / mol·dm^{-3}	η_r	C / mol·dm^{-3}	η_r
D-(+)-Maltose Monohydrate			
m_B/mol·kg^{-1} = 0.49850[a]			
at 288.15 K	η_o/mPa·s = 1.2662[b]		
0.05106	1.0862	0.10203	1.1723
0.07089	1.1199	0.49116	1.8301
at 298.15 K	η_o/mPa·s = 0.9796		
0.05096	1.0841	0.10180	1.1681
0.07074	1.1168	0.48960	1.8094
at 308.15 K	η_o/mPa·s = 0.8523		
0.05075	1.0783	0.10139	1.1566
0.07045	1.1088	0.48734	1.7539
at 318.15 K	η_o/mPa·s = 0.7339		
0.05048	1.0680	0.10081	1.1360
0.07006	1.0945	0.48363	1.6547
m_B/mol·kg^{-1} = 0.99705			
at 288.15 K	η_o/mPa·s = 2.2590		
0.05461	1.1252	0.10515	1.2413
0.07569	1.1737	0.15201	1.3488
0.08750	1.2009		
at 298.15 K	η_o/mPa·s = 1.7094		
0.05429	1.1187	0.10453	1.2286
0.07525	1.1644	0.15110	1.3306
0.08699	1.1902		
at 308.15 K	η_o/mPa·s = 1.4271		
0.05390	1.1111	0.10284	1.2141
0.07470	1.1541	0.14995	1.3095
0.08635	1.1781		
at 318.15 K	η_o/mPa·s = 1.2310		
0.05332	1.0915	0.10257	1.1763
0.07388	1.1269	0.14815	1.2549
0.08538	1.1467		
D-(+)-Lactose Monohydrate			
m_B/mol·kg^{-1} = 0.49850			
at 288.15 K			
0.05036	1.0749	0.12115	1.1800
0.07045	1.1047	0.15098	1.2243
0.09059	1.1346	0.20105	1.2988
at 298.15 K			
0.05025	1.0665	0.12089	1.1599
0.07030	1.0929	0.15064	1.1993
0.09040	1.1196	0.20058	1.2654
at 308.15 K			
0.05004	1.0594	0.12038	1.1431
0.07002	1.0831	0.15000	1.1783
0.09002	1.1070	0.19971	1.2374
at 318.15 K			
0.04978	1.0543	0.11970	1.1310
0.06963	1.0759	0.14913	1.1632
0.08953	1.0979	0.19852	1.2173
m_B/mol·kg^{-1} = 0.99705			
at 288.15 K			
0.05297	1.0998	0.10435	1.1965
0.07107	1.1337	0.14959	1.2817
0.09721	1.1830		
at 298.15 K			
0.05267	1.0833	0.10373	1.1643
0.07065	1.1119	0.14868	1.2355
0.09664	1.1531		
at 308.15 K			
0.05229	1.0703	0.10298	1.1384
0.07015	1.0942	0.14759	1.1983
0.09594	1.1289		
at 318.15 K			
0.05175	1.0629	0.10188	1.1238
0.06941	1.0843	0.14597	1.1773
0.09492	1.1153		
Sucrose			
m_B/mol·kg^{-1} = 0.49850			
at 288.15 K			
0.05001	1.0418	0.15043	1.1256

Table 3 Continued

$\frac{C}{\text{mol}\cdot\text{dm}^{-3}}$	η_r	$\frac{C}{\text{mol}\cdot\text{dm}^{-3}}$	η_r
0.07157	1.0597	0.20117	1.1680
0.10396	1.0868		
at 298.15 K			
0.04991	1.0398	0.15013	1.1195
0.07142	1.0567	0.20074	1.1598
0.10375	1.0826		
at 308.15 K			
0.04971	1.0365	0.14948	1.1100
0.07113	1.0523	0.19985	1.1471
0.10331	1.0759		
at 318.15 K			
0.04944	1.0313	0.14862	1.0945
0.07074	1.0449	0.19867	1.1263
0.10273	1.0653		
m_B/mol·kg^{-1} = 0.99705			
at 288.15 K			
0.05152	1.0737	0.15612	1.2125
0.07055	1.1011	0.20535	1.2795
0.10302	1.1476		
at 298.15 K			
0.05123	1.0697	0.15523	1.2006
0.07015	1.0956	0.20418	1.2640
0.10244	1.1394		
at 308.15 K			
0.05085	1.0591	0.15401	1.1706
0.06963	1.0811	0.20251	1.2242
0.10166	1.1185		
at 318.15 K			
0.05033	1.0505	0.15237	1.1456
0.06891	1.0693	0.20031	1.1916
0.10060	1.1012		
D-(+)-Cellobiose			
m_B/mol·kg^{-1} = 0.49850			
at 288.15 K			
0.05036	1.0186	0.09222	1.0341
0.07121	1.0263	0.15278	1.0565
at 298.15 K			
0.05026	1.0159	0.09201	1.0291
0.07105	1.0225	0.15241	1.0482
at 308.15 K			
0.05005	1.0081	0.09162	1.0148
0.07075	1.0115	0.15173	1.0246
at 318.15 K			
0.04978	1.0006	0.09089	1.0012
0.07036	1.0009	0.15084	1.0020
m_B/mol·kg^{-1} = 0.99705			
at 288.15 K			
0.05019	1.0578	0.09196	1.1057
0.07130	1.0821	0.15501	1.1784
at 298.15 K			
0.04990	1.0539	0.09142	1.0990
0.07088	1.0768	0.15406	1.1670
at 308.15 K			
0.04955	1.0465	0.09076	1.0854
0.07038	1.0662	0.15293	1.1441
at 318.15 K			
0.04903	1.0421	0.08977	1.0774
0.06963	1.0599	0.15120	1.1303

[a] m_B = molality of ammonium sulfate in water. [b] Viscosity of cosolute in water.

tration range of the disaccharides, respectively. As an appreciable concentration dependence of $V_{2,\phi}$ data was observed in all the cases, the standard partial molar volumes ($V_2^{\infty} = V_{2,\phi}^{\infty}$) at infinite dilution were evaluated by the least-squares fitting of the following equation to the corresponding data

$$V_{2,\varphi} = V_2^{\infty} + S_v m \qquad (3)$$

The slope S_v and V_2^{∞} values along with their standard deviations are summarized in Table 2. V_2^{∞} values for the studied disaccharides in water are included from an earlier work.[10,14] By using the earlier data,[10] the partial molar volumes for D-(+)-maltose and D-(+)-lactose have been calculated in the anhydrous state from their hydrated salts (maltose monohydrate and lactose monohydrate) by applying the molality correction. The values agree well with the earlier reported[14] results. No volume data for these disaccharides in aqueous $(NH_4)_2SO_4$ solutions are available in the literature for comparison.

Table 4. Viscosity *B*-Coefficients for Disaccharides in Water and in Aqueous Solutions of Ammonium Sulfate at Different Temperatures

	B-coefficient$\cdot 10^3$/m$^3\cdot$mol^{-1}		
disaccharide	water[b]	$0.49850m_B$	$0.99705m_B$
at 288.15 K			
D-(+)-maltose monohydrate	1.121 ± [a]0.001	1.690 ± 0.004	2.295 ± 0.003
D-(+)-lactose monohydrate	1.080 ± 0.002	1.486 ± 0.001	1.883 ± 0.003
sucrose	1.031 ± 0.001	0.835 ± 0.002	1.392 ± 0.004
D-(+)-cellobiose	0.901 ± 0.002	0.370 ± 0.001	1.151 ± 0.001
at 298.15 K			
D-(+)-maltose monohydrate	1.114 ± 0.001 [c](0.91)	1.653 ± 0.001	2.186 ± 0.003
D-(+)-lactose monohydrate	1.075 ± 0.002	1.322 ± 0.001	1.584 ± 0.003
sucrose	1.006 ± 0.001	0.796 ± 0.004	1.322 ± 0.002
D-(+)-cellobiose	0.885 ± 0.001	0.316 ± 0.001	1.083 ± 0.002
at 308.15 K			
D-(+)-maltose monohydrate	1.069 ± 0.001	1.547 ± 0.002	2.070 ± 0.003
D-(+)-lactose monohydrate	1.030 ± 0.001	1.188 ± 0.002	1.344 ± 0.001
sucrose	0.970 ± 0.002	0.735 ± 0.003	1.132 ± 0.004
D-(+)-cellobiose	0.850 ± 0.004	0.162 ± 0.001	0.941 ± 0.002
at 318.15 K			
D-(+)-maltose monohydrate	0.997 ± 0.001	1.353 ± 0.001	1.718 ± 0.002
D-(+)-lactose monohydrate	0.974 ± 0.002	1.093 ± 0.005	1.215 ± 0.002
sucrose	0.911 ± 0.001	0.635 ± 0.003	0.977 ± 0.003
D-(+)-cellobiose	0.796 ± 0.002	0.013 ± 0.001	0.861 ± 0.004

[a] Standard deviation. [b] Ref 10. [c] Ref 18.

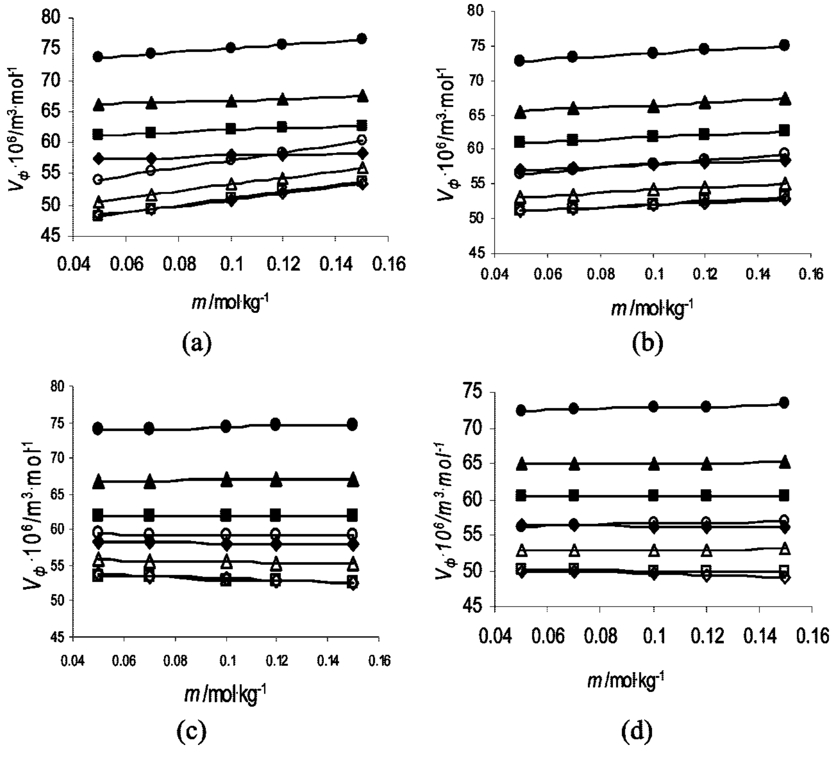


Figure 2. Apparent molar volumes, V_ϕ, of $(NH_4)_2SO_4$ versus molalities, m, of the disaccharides (a) D-(+)-maltose monohydrate, (b) D-(+)-lactose monohydrate, (c) sucrose, and (d) D-(+)-cellobiose at ◇, 288.15 K; □, 298.15 K; △, 308.15 K; and ○, 318.15 K for $0.49850m_B$ and at ◆, 288.15 K; ■, 298.15 K; ▲, 308.15 K; and ●, 318.15 K for $0.99705m_B$.

The standard partial molar volumes of transfer, $\Delta_t V_2^\infty$, at infinite dilution of each disaccharide from water to aqueous ammonium sulfate solutions were determined as

$$\Delta_t V_2^\infty = V_2^\infty[\text{in aqueous solutions of } (NH_4)_2SO_4] - V_2^\infty[\text{in water}] \quad (4)$$

The viscosity data were used to calculate the relative viscosities, η_r, from the ratio of the viscosities of the solution, η, to those of the corresponding solvent, η_o; i.e., $\eta_r = \eta/\eta_o$. The η_r values are summarized in Table 3. The viscosity *B*-coefficients were calculated by fitting the η_r values to the following Jones–Dole equation by a least-squares method

$$\eta_r = 1 + Bc \quad (5)$$

where c is the molarity of the solution (calculated from molality and density data). The *B*-coefficient values are summarized in Table 4 along with the literature values.[10,18] Transfer viscosity *B*-coefficients, $\Delta_t B$, have been calculated using the equation analogous to that used for $\Delta_t V_2^\infty$ values. The refractive index values, n_D, for various solutions are presented in Table 5.

From the dependence of $\Delta_t V_2^\infty$ values (Figure 1) on concentration of cosolute $(NH_4)_2SO_4$, it can be observed that $\Delta_t V_2^\infty$ values for D-(+)-maltose monohydrate, sucrose, and D-(+)-

Table 5. Refractive Indices, n_D, for Disaccharides in Aqueous Solutions of Ammonium Sulfate

m	temperature/K			
mol·kg^{-1}	288.15	298.15	308.15	318.15
	n_D			
	D-(+)-Maltose Monohydrate			
	m_B/mol·kg^{-1} = 0.49850			
0.00000	1.344	1.343	1.341	1.339
0.04928	1.368	1.366	1.365	1.361
0.06950	1.369	1.367	1.365	1.362
0.10055	1.370	1.368	1.366	1.364
0.53310	1.386	1.385	1.384	1.381
0.82350	1.397	1.396	1.395	1.393
1.23154	1.411	1.409	1.408	1.406
	m_B/mol·kg^{-1} = 0.99705			
0.00000	1.352	1.351	1.349	1.347
0.05164	1.378	1.376	1.374	1.372
0.07194	1.379	1.377	1.376	1.375
0.08340	1.379	1.377	1.376	1.375
0.10065	1.380	1.379	1.377	1.375
0.14717	1.382	1.381	1.380	1.378
	D-(+)-Lactose Monohydrate			
	m_B/mol·kg^{-1} = 0.49850			
0.04902	1.366	1.365	1.364	1.360
0.06891	1.367	1.365	1.364	1.362
0.08902	1.369	1.367	1.365	1.363
0.11992	1.371	1.370	1.369	1.367
0.15050	1.373	1.372	1.370	1.367
0.20280	1.375	1.372	1.371	1.370
	m_B/mol·kg^{-1} = 0.99705			
0.05009	1.376	1.374	1.372	1.372
0.06747	1.377	1.376	1.375	1.372
0.09286	1.377	1.376	1.375	1.373
0.09984	1.379	1.378	1.376	1.374
0.14470	1.380	1.379	1.378	1.376
	Sucrose			
	m_B/mol·kg^{-1} = 0.49850			
0.04864	1.364	1.363	1.361	1.359
0.06994	1.366	1.365	1.363	1.360
0.10231	1.367	1.366	1.364	1.362
0.14957	1.368	1.367	1.365	1.363
0.20226	1.369	1.368	1.366	1.363
	m_B/mol·kg^{-1} = 0.99705			
0.04863	1.373	1.371	1.369	1.367
0.06687	1.374	1.372	1.371	1.369
0.09835	1.375	1.373	1.372	1.370
0.15080	1.376	1.374	1.373	1.370
0.20054	1.376	1.375	1.374	1.372
	D-(+)-Cellobiose			
	m_B/mol·kg^{-1} = 0.49850			
0.04897	1.360	1.358	1.357	1.354
0.06963	1.361	1.360	1.358	1.357
0.09044	1.362	1.361	1.360	1.357
0.15175	1.365	1.364	1.362	1.360
	m_B/mol·kg^{-1} = 0.99705			
0.04368	1.370	1.368	1.367	1.363
0.06755	1.371	1.370	1.369	1.365
0.08750	1.372	1.371	1.369	1.367
0.14525	1.373	1.372	1.371	1.369

lactose monohydrate are positive, which increase almost linearly with concentration of $(NH_4)_2SO_4$ at the four temperatures studied, and the values also increase with temperature. In the case of D-(+)-cellobiose (Figure 1), both negative and positive $\Delta_t V_2^\infty$ values have been observed. The negative magnitude of $\Delta_t V_2^\infty$ increases sharply at lower concentrations of $(NH_4)_2SO_4$, and this increase becomes lesser at higher concentrations at (288.15 and 298.15) K. The $\Delta_t V_2^\infty$ values remain almost constant at 308.15 K having small negative magnitude. The transfer volumes are positive, and their magnitude increases with concentration of cosolute at 318.15 K. The $\Delta_t V_2^\infty$ values increase with temperature in the case of D-(+)-cellobiose also. Recently, we have reported[10] positive $\Delta_t V_2^\infty$ values for the D-(+)-maltose monohydrate and sucrose and negative values for D-(+)-cellobiose, whereas both positive and negative values were found for D-(+)-lactose monohydrate in aqueous sodium sulfate solutions studied at (288.15, 298.15, 308.15, and 318.15) K. Presently, the magnitude of $\Delta_t V_2^\infty$ values in the case of $(NH_4)_2SO_4$ at any temperature decreases for the various disaccharides in the following order: D-(+)-maltose monohydrate > D-(+)-lactose monohydrate > sucrose > D-(+)-cellobiose. The peculiar dependence of $\Delta_t V_2^\infty$ on the temperature and concentration of $(NH_4)_2SO_4$ reflects a prominent difference in the nature of hydration characteristics of various disaccharides studied.

The case of D-(+)-maltose monohydrate and D-(+)-lactose monohydrate in which water does not ligate to sugar needs further scrutiny of the results. Therefore, in the study of these, where sugar monohydrate is dissolved in the stock solution of ammonium sulfate, it adds water to the original stock solution as well as sugar. This results in a situation where each solution, in principle, has a different stock solution. Thus corrections have been applied to the molality of sugar solutions as well as of stock solutions as follows. Molar volumes of the two stock solutions used in the present study have been calculated by the method reported by Fucaloro et al.[1] from their densities and compositions. By assuming linearity of molar volumes with respect to mole fraction of salt, the expected density for each of the stock solutions has been calculated as water is added through the addition of the monohydrate of sugar. Then we have recalculated the apparent molar volumes for each maltose and lactose solution at 298.15 K in the presence of 0.99705 mol·kg^{-1} of ammonium sulfate solution using the corrected molalities and corrected densities for stock solution. From these data, the partial molar volumes at infinite dilution have been calculated (Table 2). The partial molar volumes of transfer at infinite dilution for the maltose and lactose (in the anhydrous state) obtained from their hydrated salts are ($10.43 \cdot 10^{-6}$ and $9.95 \cdot 10^{-6}$) m^3·mol^{-1}, respectively, by applying molality corrections. Their corresponding values for maltose and lactose without applying correction are ($10.20 \cdot 10^{-6}$ and $9.79 \cdot 10^{-6}$) m^3·mol^{-1}, respectively. It may be seen that the difference in the transfer volumes obtained by two approaches is very small and does not affect the conclusions derived from the results without applying corrections. But this approach will provide reliable partial molar volumes for the salts in the anhydrous state from studies of hydrated salts.

The volumetric data obtained for the disaccharides can be rationalized by taking into consideration the effects of solute and cosolute on the structure of water and interactions operating between them. The following types of interactions are possible between solute (disaccharide) and cosolute $(NH_4)_2SO_4$. (1) Hydrophilic−ionic interactions between the hydrophilic sites (−OH, −C═O, and −O−) of the disaccharides and the ions (NH_4^+/SO_4^{2-}) of the cosolute. (2) Hydrophobic−ionic interactions between the hydrophobic parts of the disaccharide molecules and the ions of the cosolute. According to the cosphere overlap model,[19,20] the first type of interactions contribute positively, whereas the second type of interactions make negative contributions to $\Delta_t V_2^\infty$ values. The positive $\Delta_t V_2^\infty$ values for D-(+)-lactose monohydrate, D-(+)-maltose monohydrate, and sucrose (at all temperatures studied) and D-(+)-cellobiose (at 318.15 K only) indicate that the hydrophilic−ionic interactions predominate over the hydrophobic−ionic interactions. The increase in $\Delta_t V_2^{\infty}$ values with concentration of $(NH_4)_2SO_4$ points toward a strengthening of the hydrophilic—ionic interactions over the whole concentration range. The negative $\Delta_t V_2^{\infty}$ values obtained in the case of D-(+)-cellobiose at (288.15, 298.15, and 308.15) K indicate the dominance of hydrophobic—ionic interactions over those of hydrophilic—ionic interactions. It may be noted that the negative magnitude of $\Delta_t V_2^{\infty}$ decreases with temperature, and the $\Delta_t V_2^{\infty}$ values are positive at 318.15 K. This suggests that the negative contribution to $\Delta_t V_2^{\infty}$ from hydrophobic—ionic interactions decreases and that the positive contribution from hydrophilic—ionic interactions increases with the rise of temperature in the case of D-(+)-cellobiose.

Earlier, we have also reported[10,12–14] significant positive values of $\Delta_t V_2^{\infty}$, $\Delta_t C_{P,2}^{\infty}$, $\Delta_t B$, and $\Delta_t K_{S,2}^{\infty}$ for saccharides and polyols in the presence of various electrolytes, where hydrophilic—ionic interactions dominate over the hydrophobic—ionic interactions. Whereas, a study[11] of saccharides in the presence of tetra-*n*-alkylammonium bromides suggested that hydrophobic—hydrophobic, hydrophobic—ionic, hydrophilic—ionic, and hydrophilic—hydrophobic interactions occur due to the hydrophobic nature of alkylammonium salts.

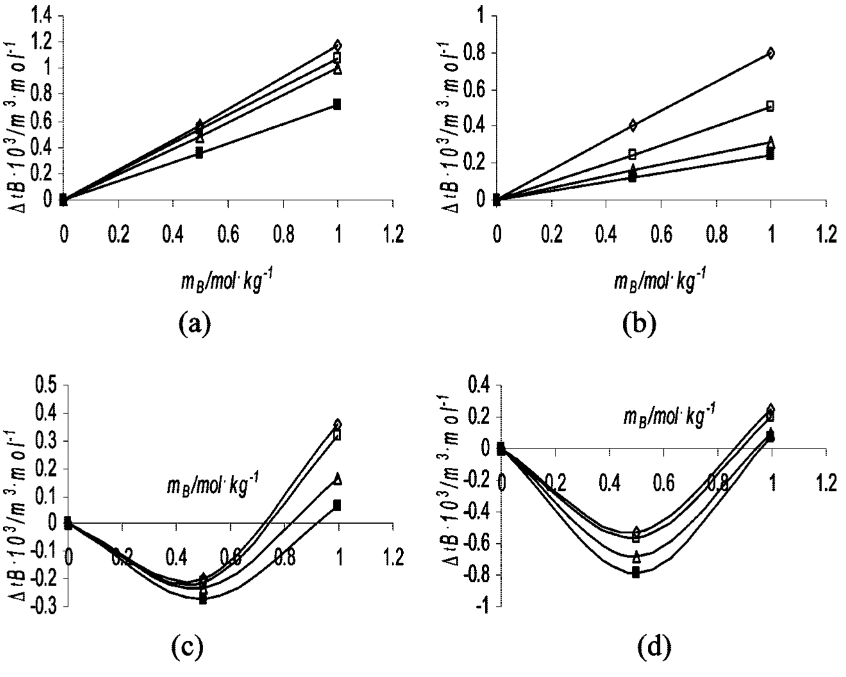
High concentrations of ammonium sulfate promote protein binding, whereas moderate concentration results in elution of the bound proteins and has been explained by its salting-out effect on proteins.[16] Therefore, ammonium sulfate like sodium sulfate can also be a good probe to distinguish the hydration behavior of the disaccharides studied which have salting-in and salting-out effects on proteins. This has actually been observed, as the $\Delta_t V_2^{\infty}$ values differ largely for the studied disaccharides and further $\Delta_t V_2^{\infty}$ values also differ both in sign and magnitude for these disaccharides in the cases of Na_2SO_4[10] and $(NH_4)_2SO_4$.

According to Shahidi's equation,[21] the standard partial molar volume of a saccharide molecule at infinite dilution can be represented as

$$V_2^{\infty} = V_{v.w} + V_{void} - V_{shrinkage} \tag{6}$$

where $V_{v.w}$ is the van der Waals volume; V_{void} is the associated void or empty volume; and $V_{shrinkage}$ is the shrinkage in volume caused by interaction of a hydrogen bonding group with water molecules. If we assume that $V_{v.w}$ and V_{void} have the same magnitudes in water and aqueous ammonium sulfate solutions, the positive $\Delta_t V_2^{\infty}$ values accompanying the transfer of disaccharides can be attributed to the decrease in the volume of shrinkage in ammonium sulfate solutions, whereas the reverse may be true for the negative $\Delta_t V_2^{\infty}$ values. Both positive and negative $\Delta_t V_2^{\infty}$ values observed in these cases suggest that there is a strong competition between various interactions occurring in these solutions which depend on the nature of the disaccharide as well as upon the temperature of the solution and concentration of the cosolute, $(NH_4)_2SO_4$.

To analyze the data further, the apparent molar volume V_{ϕ} values of $(NH_4)_2SO_4$ in aqueous solutions of disaccharides have also been determined. For the determination of apparent molar volumes for ammonium sulfate in aqueous sugar solutions, we have fitted the density data for sugars in water (ref 10) as a function of molality of sugars and then recalculated the density at rounded molalities (as shown in Figure 2) which will be the density of solvent in this case. Then, we also fitted the density data for the ternary solution (sugar + ammonium sulfate + water) and recalculated the density data at the above rounded molalities of the sugars. These densities will act as densities for solutions. Then, at fixed concentration of ammonium sulfate (at (0.49850 and 0.99705)m_B), the apparent molar volumes at different concentrations of sugar have been calculated. These values have an uncertainty of the order of $\pm\ 0.11 \cdot 10^6\ m^3 \cdot mol^{-1}$. The plots of V_{ϕ} versus concentration of disaccharide (Figure 2) show positive slopes for D-(+)-maltose monohydrate and D-(+)-lactose monohydrate. For sucrose, the V_{ϕ} values remain almost constant at 0.99705m_B, whereas the values slightly decrease at 0.49850m_B at lower temperatures, i.e., (288.15, 298.15, and 308.15) K. For D-(+)-cellobiose, the V_{ϕ} values remain constant at both the concentrations of cosolute and temperatures (288.15, 298.15, and 308.15) K, and the values start increasing at 318.15 K. Parallel discussion in Na_2SO_4[10] shows a decrease in V_{ϕ} values with the concentration of D-(+)-cellobiose, and at 318.15 K, the values start increasing. This



(a) (b) (c) (d)

Figure 3. Viscosity *B*-coefficients of transfer, $\Delta_t B$, of disaccharides (a) D-(+)-maltose monohydrate, (b) D-(+)-lactose monohydrate, (c) sucrose, and (d) D-(+)-cellobiose versus molalities, m_B, of $(NH_4)_2SO_4$ at ◇, 288.15 K; □, 298.15 K; Δ, 308.15 K; ■, 318.15 K.

may be the reason that D-(+)-cellobiose has more negative $\Delta_t V_2^{\infty}$ values in the presence of Na_2SO_4 than in $(NH_4)_2SO_4$. These observations show a peculiar hydration behavior of D-(+)-cellobiose in comparison to other disaccharides specific to both the concentration of cosolute (Na_2SO_4/$(NH_4)_2SO_4$) and temperature. Further, an appreciable difference between the $\Delta_t V_2^{\infty}$ values is certainly due to difference in stereochemical structure and hence the difference in strength of interactions of disaccharides with cosolute (Na_2SO_4/$(NH_4)_2SO_4$) in these solutions.

High positive values of $\Delta_t V_2^{\infty}$ obtained for D-(+)-maltose monohydrate and negative $\Delta_t V_2^{\infty}$ values for D-(+)-cellobiose at (288.15, 298.15, and 308.15) K in both the cosolutes (Na_2SO_4 and $(NH_4)_2SO_4$) suggest the difference in hydration characteristics of these disaccharides. D-(+)-Maltose monohydrate has stronger interactions with cosolute than D-(+)-cellobiose which may be due to a more flexible $\alpha 1 \rightarrow 4$ glycosidic bond present in D-(+)-maltose monohydrate than the $\beta 1 \rightarrow 4$ glycosidic bond in D-(+)-cellobiose, although both contain the same type of subunits. This observation is also supported by Neal and Goring[22] on the basis of expansibility data that the folding of D-(+)-maltose monohydrate is more than in D-(+)-cellobiose due to hydrophobic interactions. Brown et al. have also reported[2] a similar type of behavior for D-(+)-maltose monohydrate and D-(+)-cellobiose. Calorimetric and densitymetric studies[23] also show selectivity in binding with crown ethers for D-(+)-cellobiose and D-(+)-maltose monohydrate in dilute aqueous solutions. These observations also get support from our earlier reported studies.[10,12]

The expansion coefficients $(\partial V_2^{\infty}/\partial T)_P$ have been calculated by fitting the V_2^{∞} data into the following equation.

$$V_2^{\infty} = v_o + v_1 T + v_2 T^2 \tag{7}$$

where v_o, v_1, and v_2 are constants and their values are given in Table 6 along with standard deviations and correlation coefficients. The $(\partial V_2^{\infty}/\partial T)_P$ values are positive in all cases. All the disaccharides show an appreciable increase in $(\partial V_2^{\infty}/\partial T)_P$ values with temperature at both the concentrations of $(NH_4)_2SO_4$. D-(+)-Maltose monohydrate shows an exceptionally larger increase (almost double) than D-(+)-lactose monohydrate and sucrose at $0.99705m_B$. On the contrary, D-(+)-maltose monohydrate shows a decrease in $(\partial V_2^{\infty}/\partial T)_P$ values at both the concentrations of Na_2SO_4, and the decrease is sharp at $0.99705m_B$. In the case of D-(+)-lactose monohydrate, the values increase at $0.49850m_B$ but remain constant at $0.99705m_B$ Na_2SO_4, whereas in sucrose, the values show an increase at both concentrations of Na_2SO_4. D-(+)-Cellobiose shows an exceptionally large increase in $(\partial V_2^{\infty}/\partial T)_P$ values at both the concentrations of Na_2SO_4 studied.[10]

Hepler[24] proposed the equation $(\partial C_{P,2}^{\infty}/\partial P)_T = -T(\partial^2 V_2^{\infty}/\partial T^2)_P$, by which qualitative information on hydration of a solute could be obtained from the thermal expansion of aqueous solutions. For a structure breaking solute, the left side of the equation should be positive and $(\partial^2 V_2^{\infty}/\partial T^2)_P$ consequently should be negative for structure breaking solute and positive for structure making solute. The positive $(\partial^2 V_2^{\infty}/\partial T^2)_P$ values (obtained from eq 7) of disaccharides in water and the increase in these values with the concentration of $(NH_4)_2SO_4$ suggest that the disaccharides behave as structure makers. A similar type of behavior was observed[10] for D-(+)-cellobiose, sucrose, and D-(+)-lactose monohydrate in the case of Na_2SO_4 except D-(+)-maltose monohydrate.

The plots of viscosity (plots not shown), η, versus concentration indicate that the viscosity is greatly influenced by the temperature and cosolute concentration. It has been noticed that the η values increase with the concentration of disaccharide and $(NH_4)_2SO_4$; however, they decreases with the rise of temperature. The viscosity *B*-coefficient is an empirical term, which depends upon solute−solvent interactions and on the relative size of the solute and solvent molecules. The positive and negative values of the viscosity *B*-coefficients of an ion in water represent the structure-making and -breaking abilities,[25] respectively. Positive viscosity *B*-coefficients are obtained (Table 4) for all of the disaccharides studied at both concentrations of $(NH_4)_2SO_4$, whereas both positive and negative $\Delta_t B$ values (Figure 3) were observed for the studied systems. Large positive $\Delta_t B$ values have been obtained for D-(+)-lactose monohydrate and D-(+)-maltose monohydrate. The magnitude of $\Delta_t B$ values

Table 6. Values of Algebraic Coefficients of Equation 7

D-(+)-Maltose monohydrate

v_o	v_1	v_2	[b]SD	[c]R^2
[a]In water				
195.23	0.0656	0.00015	0.004	1
In $0.49850m_B$ $(NH_4)_2SO_4$				
678.42	−3.3044	0.00608	0.498	0.99662
In $0.99705m_B$ $(NH_4)_2SO_4$				
2623.16	−16.5598	0.02870	1.856	0.99117

D-(+)-Lactose monohydrate

v_o	v_1	v_2	[b]SD	[c]R^2
[a]In water				
177.07	0.2049	−0.00012	0.029	0.99990
In $0.49850m_B$ $(NH_4)_2SO_4$				
637.94	−3.0034	0.00550	0.389	0.99731
In $0.99705m_B$ $(NH_4)_2SO_4$				
1088.97	−6.1701	0.01110	1.131	0.99214

Sucrose

v_o	v_1	v_2	SD	R^2
[a]In water				
302.37	−0.6761	0.00125	0.013	0.99995
In $0.49850m_B$ $(NH_4)_2SO_4$				
791.23	−4.1198	0.00733	0.244	0.99890
In $0.99705m_B$ $(NH_4)_2SO_4$				
1069.29	−6.1401	0.01100	1.467	0.98536

D-(+)-Cellobiose

v_o	v_1	v_2	SD	R^2
[a]In water				
182.81	0.0807	0.00005	0.000	1
In $0.49850m_B$ $(NH_4)_2SO_4$				
267.82	−0.8693	0.00222	0.159	0.99978
In $0.99705m_B$ $(NH_4)_2SO_4$				
1485.55	−9.0437	0.01595	1.892	0.98297

[a] Ref 10. [b] Standard deviation. [c] Correlation coefficients.

Table 7. *dB/dT* Values for Disaccharides in Aqueous Ammonium Sulfate Solutions

	dB/dT		
	$dm^3 \cdot K^{-1} \cdot mol^{-1}$		
disaccharides	[a]water	$0.49850m_B$ $(NH_4)_2SO_4$	$0.99705m_B$ $(NH_4)_2SO_4$
D-(+)-maltose monohydrate	−0.0042	−0.0112	−0.0185
D-(+)-lactose monohydrate	−0.0036 [b](−0.005)	−0.0131	−0.0224
sucrose	−0.0040	−0.0066	−0.0144
D-(+)-cellobiose	−0.0035	−0.0123	−0.0101

[a] Ref 10. [b] Ref 18.

Table 8. Activation Gibbs Free Energy, $\Delta\mu_2^{\infty\ddagger}$, for Viscous Flow of Disaccharides in Water and Aqueous Solutions of Ammonium Sulfate

	$\Delta\mu_2^{\infty\ddagger}$/kJ·mol^{-1}			
	temperature/K			
disaccharides	288.15	298.15	308.15	318.15
	[a]water			
D-(+)-maltose monohydrate	186.24	190.97	190.11	184.82
D-(+)-lactose monohydrate	180.67	185.46	184.40	181.23
sucrose	172.24	173.91	173.70	169.76
D-(+)-cellobiose	154.80	157.21	156.68	152.99
	0.49850m_B $(NH_4)_2SO_4$			
D-(+)-maltose monohydrate	246.23	249.39	242.77	223.42
D-(+)-lactose monohydrate	220.68	206.63	195.02	187.71
sucrose	137.67	136.79	132.88	123.17
D-(+)-cellobiose	78.58	74.17	56.33	37.97
	0.99705m_B $(NH_4)_2SO_4$			
D-(+)-maltose monohydrate	332.94	328.05	321.44	281.79
D-(+)-lactose monohydrate	279.93	248.48	222.74	210.77
sucrose	214.59	211.12	191.58	174.97
D-(+)-cellobiose	182.39	178.66	164.29	158.12

[a] Ref 10.

Table 9. Thermodynamic Activation Parameter of Transfer, ΔG_2^∞ (1−1′), for the Disaccharides from Ground to Transition State in Aqueous Solutions of Ammonium Sulfate

	ΔG_2^∞ (1−1′)/kJ·mol^{-1}			
	temperature/K			
disaccharides	288.15	298.15	308.15	318.15
	[a]water			
D-(+)-maltose monohydrate	176.80	181.81	181.18	176.09
D-(+)-lactose monohydrate	171.23	176.30	175.47	172.50
sucrose	162.80	164.75	164.77	161.03
D-(+)-cellobiose	145.36	148.05	147.75	144.26
	0.49850m_B $(NH_4)_2SO_4$			
D-(+)-maltose monohydrate	236.38	239.83	233.23	213.95
D-(+)-lactose monohydrate	210.83	197.07	185.48	178.24
sucrose	127.82	127.23	123.34	113.70
D-(+)-cellobiose	58.88	64.61	46.79	28.50
	0.99705m_B $(NH_4)_2SO_4$			
D-(+)-maltose monohydrate	321.77	317.17	310.64	271.01
D-(+)-lactose monohydrate	268.76	237.60	211.94	199.99
sucrose	203.42	200.24	180.78	164.19
D-(+)-cellobiose	171.22	167.78	153.49	147.34

[a] Ref 10.

decreases with the rise of temperature. D-(+)-Cellobiose and sucrose show a significant decrease in $\Delta_t B$ values at 0.49850m_B. After passing through minima (at ≈ 0.50m_B), the values become positive at 0.99705m_B. A large difference in $\Delta_t B$ values is again in consonance with the earlier observations made on the $\Delta_t V_2^\infty$ basis that D-(+)-maltose monohydrate and D-(+)-cellobiose have different hydration characteristics. Similarly, we have reported[10] a significant fall in $\Delta_t B$ for D-(+)-cellobiose in comparison to other disaccharides at 0.49850m_B and large positive values for D-(+)-maltose monohydrate in the presence of Na_2SO_4. The positive $\Delta_t B$ values suggest that an overall structural increase occurs, whereas negative values suggest that a structural decrease occurs in the solution.

The negative magnitude of dB/dT values (Table 7) increases with an increase in concentration of $(NH_4)_2SO_4$, and similar is the case[10] in the presence of Na_2SO_4. It reinforces the conclusion drawn from $\Delta_t V_2^\infty$ and $\Delta_t B$ results that disaccharides are structure makers.

The average Gibbs energy of activation of a solute for a viscous flow in a solvent, $\Delta\mu_1^{\infty\ddagger}$, can be calculated from the following equation proposed by Eyring and co-workers.[26]

$$\eta_o = [hN_A/V^\infty_{1,\phi}]\exp[\Delta\mu_1^{\infty\ddagger}/RT] \qquad (8)$$

where h and N_A are the Planck's constant and Avogadro's number, respectively, and $V^\infty_{1,\phi}$ is the average molar volume of the aqueous $(NH_4)_2SO_4$ solutions at (288.15, 298.15, 308.15, and 318.15) K (calculated from density data). The resulting values of $\Delta\mu_1^{\infty\ddagger}$ are: (9.44, 9.16, 8.93, and 8.73) kJ·mol^{-1} for water; (9.85, 9.56, 9.54, and 9.47) kJ·mol^{-1} for aqueous solutions of $(NH_4)_2SO_4$ at 0.49850m_B; and (11.7, 10.88, 10.80, and 10.78) kJ·mol^{-1} for aqueous solutions of $(NH_4)_2SO_4$ at 0.99705m_B at (288.15, 298.15, 308.15, and 318.15) K.

According to Feakins et al.,[27,28] the activation Gibbs energy, $\Delta\mu_1^{\infty\ddagger}$ for viscous flow of disaccharides in aqueous and mixed aqueous solutions is related to the viscosity B-coefficient by the following equation.

$$B = [(V^\infty_{1,\phi} - V^\infty_2)/1000] + V^\infty_{1,\phi}[(\Delta\mu_2^{\infty\ddagger} - \Delta\mu_1^{\infty\ddagger})/1000RT] \qquad (9)$$

The $\Delta\mu_2^{\infty\ddagger}$ values obtained from the above equation for the various disaccharides in aqueous ammonium sulfate solutions at different temperatures are given in Table 8. According to transition-state theory,[27,28] every solvent molecule in one mole of solution must pass through the transition state and also interact more or less strongly with the solute molecules. Thus, $\Delta\mu_2^{\infty\ddagger}$ contains the Gibbs energy of transfer of a solute from the ground-state to the transition-state solvents, ΔG_2^∞ (1−1′), and the Gibbs energy of the solute through its own viscous transition state, ΔG_2^∞ (2−2′). The ΔG_2^∞ (1−1′) values (Table 9) have been obtained from the $\Delta\mu_2^{\infty\ddagger}$ values, as ΔG_2^∞ (2−2′) values are taken equal to $\Delta\mu_1^{\infty\ddagger}$.

The $\Delta\mu_2^{\infty\ddagger}$ and ΔG_2^∞ (1−1′) values are positive and much larger than the $\Delta\mu_1^{\infty\ddagger}$, which suggests that the formation of the transition state is less favored in the presence of the disaccharides. The ΔG_2^∞ (1−1′) values for various disaccharides increase with concentration of cosolute and decrease with rise of temperature and follow the order: D-(+)-maltose monohydrate > D-(+)-lactose monohydrate > sucrose > D-(+)-cellobiose. It indicates that a greater amount of energy is required to cause the transfer from the ground-state solvent to the transition-state solvent for D-(+)-maltose monohydrate than D-(+)-cellobiose. Accordingly, more solute−solvent bonds must be broken to form the transition state. Thus, from these observations, it may be inferred that the formation of the transition state becomes less favored in the case of D-(+)-maltose monohydrate. Similarly, high ΔG_2^∞ (1−1′) values have been reported[10] for D-(+)-maltose monohydrate in the presence of Na_2SO_4.

The refractive index, n_D, values (Table 5) show an increase with increase in concentration of solute and cosolute but decrease with increase in temperature. The magnitude of n_D values (Table 5) is more for D-(+)-maltose monohydrate and smaller for D-(+)-cellobiose in comparison to other two disaccharides in $(NH_4)_2SO_4$ and Na_2SO_4. This behavior is in good agreement with the inference obtained from our volumetric and rheological data. These studies again reflect that the solute−cosolute interactions are stronger in the case of D-(+)-maltose monohydrate and weaker in the case of D-(+)-cellobiose.

Comparison of the results for disaccharides in aqueous $(NH_4)_2SO_4$ with the corresponding data in aqueous Na_2SO_4 solutions has been made, and the following general observations have emerged: (i) The magnitude of the V_2^∞ and $\Delta_t V_2^\infty$ for the studied disaccharides is larger in the case of $(NH_4)_2SO_4$ as cosolute than Na_2SO_4. The $\Delta_t V_2^\infty$ values in the case of $(NH_4)_2SO_4$ follow the order: D-(+)-maltose monohydrate > D-(+)-lactose monohydrate > sucrose > D-(+)-cellobiose, while in the case of Na_2SO_4, the order is: D-(+)-maltose monohydrate > sucrose > D-(+)-lactose monohydrate > D-(+)-cellobiose. (ii) The magnitude of *B*-coefficients, Δ_tB, $(\partial V_2^\infty/\partial T)_P$, and $(\partial^2V_2^\infty/\partial T^2)_P$ values are higher for D-(+)-maltose monohydrate and D-(+)-lactose monohydrate than D-(+)-cellobiose and sucrose in the presence of $(NH_4)_2SO_4$, and the reverse is true when Na_2SO_4 is the cosolute. (iii) The n_D values of all disaccharides are higher in $(NH_4)_2SO_4$ than in Na_2SO_4. (iv) The dB/dT values are more negative for D-(+)-maltose monohydrate and D-(+)-lactose monohydrate in comparison to D-(+)-cellobiose and sucrose in the presence of $(NH_4)_2SO_4$.

The larger magnitude of various parameters observed in the case of $(NH_4)_2SO_4$ indicates that the disaccharide−$(NH_4)_2SO_4$ interactions are stronger than disaccharide−Na_2SO_4 interactions. In other words, hydrophilic−hydrophilic-type interactions are more pronounced in the case of $(NH_4)_2SO_4$. In summary, the volumetric, rheological, and refractometric data show higher values for D-(+)-maltose monohydrate in both the cosolutes, whereas D-(+)-cellobiose has smaller values. This can conclude that solute−cosolute interactions are stronger in the case of D-(+)-maltose monohydrate and weaker in the case of D-(+)-cellobiose.

Literature Cited

(1) Fucaloro, A. F.; Pu, Y.; Cha, K.; Williams, A.; Conrad, K. Partial Molar Volumes and Refractions of Aqueous Solutions of Fructose, Glucose, Mannose, and Sucrose at 15.00, 20.00, and 25.00°C. *J. Solution Chem.* **2007**, *36*, 61–80.

(2) Brown, B. R.; Ziemer, S. P.; Niederhauser, T. L.; Woolley, E. M. Apparent Molar Volumes and Apparent Molar Heat Capacities of Aqueous D(+)-Cellobiose, D(+)-Maltose, and Sucrose at Temperatures (from 278.15 to 393.15) K and at the Pressure 0.35 MPa. *J. Chem. Thermodyn.* **2005**, *37*, 843–853.

(3) Bai, T.-C.; Yan, G.-B. Viscosity B-coefficients and Activation Parameters for Viscous Flow of a Solution of Heptanedioic acid in Aqueous Sucrose Solution. *Carbohydr. Res.* **2003**, *338*, 2921–2927.

(4) Longinotti, M. P.; Corti, H. R. Electrical Conductivity and Complexation of Sodium Borate in Trehalose and Sucrose Aqueous Solutions. *J. Solution Chem.* **2004**, *33*, 1029–1040.

(5) Longinotti, M. P.; Mazzobre, M. F.; Buera, M. P.; Corti, H. R. Effect of Salts on the Properties of Aqueous Sugar Systems in Relation to Biomaterial Stabilization. Part 2. Sugar crystallization Rate and Electrical Conductivity Behaviour. *Phys. Chem. Chem. Phys.* **2002**, *4*, 533–540.

(6) Miller, D. P.; Pablo, J. J. de. Calorimetric Solution Properties of Simple Saccharides and Their Significance for the Stabilization of Biological Structure and Function. *J. Phys. Chem. B* **2000**, *104*, 8876–8883.

(7) Goldberg, R. B.; Tewari, Y. B.; Ahluwalia, J. C. Thermodynamics of the Hydrolysis of Sucrose. *J. Biol. Chem.* **1989**, *264*, 9901–9904.

(8) Galema, S. A.; Engberts, J. B. F. N.; Hoiland, H.; Forland, G. M. Informative Thermodynamic Properties of the Effect of Stereochemistry on Carbohydrate Hydration. *J. Phys. Chem.* **1993**, *97*, 6885–6889.

(9) Galema, S. A.; Blandamer, M. J.; Engberts, J. B. F. N. Stereochemical Aspects of Hydration of Carbohydrates in Aqueous Solutions. 2. Kinetic Medium Effects. *J. Org. Chem.* **1992**, *57*, 1995–2001.

(10) Banipal, P. K.; Dhanjun, H. S.; Sharma, S.; Hundal, H.; Banipal, T. S. Effect of Sodium Sulphate on the Volumetric, Rheological and Refractometric Properties of Some Disaccharides in Aqueous Solutions at Different Temperatures. *Z. Phys. Chem.* **2008**, *222*, 1–28.

(11) Banipal, P. K.; Gautam, S.; Dua, S.; Banipal, T. S. Effect of Ammonium Salts on the Volumetric and Viscometric Behaviour of D(+)-Glucose, D(-)-Fructose and Sucrose in Aqueous Solutions at 25°C. *J. Solution Chem.* **2006**, *35*, 815–844.

(12) Banipal, P. K.; Banipal, T. S.; Ahluwalia, J. C.; Lark, B. S. Partial Molar Heat Capacities and Volumes of Transfer of Some Saccharides from Water to Aqueous Sodium Chloride Solutions at $T = 298.15$ K. *J. Chem. Thermodyn.* **2002**, *34*, 1825–1846.

(13) Banipal, P. K.; Kaur, G.; Banipal, T. S. Partial Molar Volumes of Transfer of Some Saccharides from Water to Aqueous Cupric Chloride and Zinc Chloride Solutions at 298.15 K. *Indian J. Chem. A* **2004**, *43*, 35–40.

(14) Banipal, P. K.; Banipal, T. S.; Lark, B. S.; Ahluwalia, J. C. Partial Molar Heat Capacities and Volumes of Some Mono-, Di- and Trisaccharides in Water at 298.15, 308.15 and 318.15 K. *J. Chem. Soc., Faraday Trans.* **1997**, *93* (1), 81–87.

(15) Wadi, R. K; Ramasami, P. Partial Molal Volumes and Adiabatic Compressibilities of Transfer of Glycine and DL-Alanine from Water to Aqueous Sodium Sulfate at 288.15, 298.15 and 308.15 K. *J. Chem. Soc., Faraday Trans.* **1997**, *93* (2), 243–247.

(16) Arakawa, T.; Tsumoto, K.; Ejima, D.; Kita, Y.; Yonezawa, Y.; Tokunaga, M. Induced Binding of Proteins by Ammonium Sulfate in Affinity and Ion-Exchange Column Chromatography. *J. Biochem. Biophys. Methods* **2007**, *70*, 493–498.

(17) Archer, D. G. Thermodynamic Properties of the Sodium Chloride + Water System. II. Thermodynamic Properties of NaCl (aq). $NaCl.2H_2O$(Cr) and Phase Equilibria. *J. Phys. Chem. Ref. Data.* **1992**, *21*, 793–829.

(18) Miyajima, K.; Sawada, M.; Nakagaki, M. Studies on Aqueous Solutions of Saccharides. II. Viscosity B-coefficients, Apparent Molar Volumes and Activity Coefficients of D-Glucose, Maltose and Maltotriose in Aqueous Solutions. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1954–1957.

(19) Gurney, R. W. *Ionic Processes in Solution*; Mc-Graw Hill: New York, 1953; Vol. 3, Chap. 1.

(20) Desnoyers, J. E.; Arel, M.; Perron, G.; Jolicoeur, C. Apparent Molal Volumes of Alkali Halides in Water at 25°C, Influence of Structural Hydration Interactions on Concentration Dependence. *J. Phys. Chem.* **1969**, *73*, 3346–3351.

(21) Shahidi, F.; Farrell, P. G.; Edward, J. T. Partial Molar Volumes of Organic Compounds in Water. III. Carbohydrates. *J. Solution Chem.* **1976**, *5*, 807–816.

(22) Neal, J. L.; Goring, D. A. Hydrophobic Folding of Maltose in Aqueous Solution. *Can. J. Chem.* **1970**, *48*, 3745–3747.

(23) Parfenyuk, E. V.; Lebedeva, N. Sh. Effect of the Type of Glycosidic Linkage on the Selective Interactions of Maltose and Cellobiose with Some Crown Ethers in Dilute Aqueous Solutions. *J. Solution Chem.* **2007**, *36*, 97–105.

(24) Hepler, L. G. Thermal Expansion and Structure in Water and Aqueous Solutions. *Can. J. Chem.* **1969**, *47*, 4613–4617.

(25) *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*; Wen, W.-Y., Horne, R. A., Eds.; Wiley: New York, 1972; Chapter 15.

(26) Glasstone, S.; Laidler, K. J.; Eyring, H. *Theory of Rate Processes*; Mc-Graw Hill: New York, 1941; p 477.

(27) Feakins, D.; Waghorne, W. E.; Lawrence, K. G. The Viscosity and Structure of Solutions - Part 1. A New Theory of the Jones-Dole B-coefficient and the Related Activation Parameters: Application to Aqueous Solutions. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 563–568.

(28) Feakins, D.; Bates, F. M.; Waghorne, W. E.; Lawrence, K. G. Relative Viscosities and Quasi Thermodynamics of Solutions of Tert-Butyl Alcohol in the Methanol-Water System: A Different View of the Alkyl-Water Interactions. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3381–3388.

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