Apparent Molar Volumes and Viscosity *B*-Coefficients of Carbohydrates in Aqueous Cetrimonium Bromide Solutions at (298.15, 308.15, and 318.15) K

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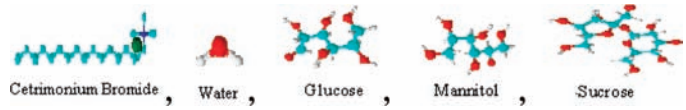
Apparent molar volumes (ϕ_V) and viscosity *B*-coefficients for some carbohydrates (D-glucose, D-mannitol, and D-sucrose) in (0.001, 0.003, and 0.005) mol·kg^{-1} aqueous cetrimonium bromide (*N*-cetyl-*N*,*N*,*N*-trimethyl ammonium bromide) ($C_{19}H_{42}BrN$) solutions have been determined from solution density, ρ, and viscosity, η, measurements at (298.15, 308.15, and 318.15) K as a function of the concentration of carbohydrates. The limiting apparent molar volume (ϕ_V^0) and experimental slopes (S_v^*) obtained from the Masson equation have been interpreted in terms of solute−solvent and solute−solute interactions, respectively. The viscosity data were analyzed using the Jones−Dole equation, and the derived parameters *A* and *B* have also been interpreted in terms of solute−solute and solute−solvent interactions, respectively, in the mixed solutions. The structure-making or -breaking ability of carbohydrates has been discussed in terms of the sign of $(\delta^2\varphi_V^0/\delta T^2)_P$ as well as d*B*/d*T*. The three-dimensional representation of the investigated molecules concerned with this paper is shown below for a better understanding.



Introduction

Carbohydrates are an exceptionally important constituent of biological systems. They play an important role in animal and plant physiology. Carbohydrates are sources of energy for vital metabolic processes. Water, the most abundant compound on earth, is widely used in chemistry as a universal solvent. It is also the most important solvent for the simpler saccharides. Cetrimonium bromide is one of the components of the topical antiseptic Cetrimide. It is also widely used as an active ingredient for hair conditioners, detergent sanitizers, disinfection agents, and softener for textiles and paper products. In this work, we have taken carbohydrates (D-glucose, D-mannitol, and D-sucrose) in (0.001, 0.003, 0.005) mol·kg^{-1} aqueous cetrimonium bromide solutions. Understanding the behavior of carbohydrates in cetrimonium bromide solution will be of utmost importance in biological and pharmaceutical science. Cetrimonium bromide forms micelles in water. Depending on the temperature and concentration of the cetrimonium bromide, water is forced to attain a specific structural form. Addition of carbohydrates to this solution will perturb the structure of the solution, which is expected to affect the volumetric and viscometric properties to a high degree.

Here, we have attempted to report the limiting apparent molar volume (ϕ_V^0), experimental slopes (S_V^*), and viscosity *B*-coefficients for the cited carbohydrates in (0.001, 0.003, and 0.005) mol·kg^{-1} aqueous cetrimonium bromide solutions given in Scheme 1.

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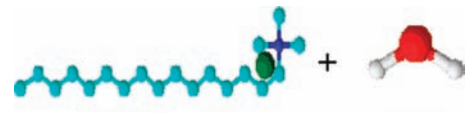
Scheme 1



Experimental Section

Materials. D-Glucose, D-mannitol, and D-sucrose (Sd. Fine Chemicals, India) were purified using standard methods[1] (mass fraction purity 0.98). Cetrimonium bromide (Thomas Baker, India, mass fraction purity 0.99) was used as such without further purification. Deionized, doubly distilled, degassed water with a specific conductance of $1\cdot10^{-6}$ S·cm^{-1} was used for the preparation of different aqueous cetrimonium bromide solutions. The physical properties of different aqueous cetrimonium bromide solutions are listed in Table 1.

Apparatus and Procedure. The density, ρ, was measured with an Anton Paar density meter (DMA 4500M).

The uncertainty in the density measurements is within ± $5\cdot10^{-4}$ g·cm^{-3}. It was calibrated by double-distilled water and dry air. The viscosity, η, was measured by means of a suspended Ubbelohde type viscometer, calibrated at the experimental temperatures with doubly distilled water and purified methanol. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed vertically in a glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch correct to ± 0.1 s. At least three repetitions of each data point reproducible to ± 0.1 s

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Table 1. Densities (ρ) and Viscosities (η) of Cetrimonium Bromide (1) + Water (2) Solutions at (298.15, 308.15, and 318.15) K

T/K	$\rho \cdot 10^{-3}$/kg·m^{-3}	η/mPa·s
	$m_1 = 0.001^a$	
298.15	0.9972	0.899
308.15	0.9942	0.744
318.15	0.9904	0.617
	$m_1 = 0.003^a$	
298.15	0.9973	0.910
308.15	0.9943	0.752
318.15	0.9905	0.622
	$m_1 = 0.005^a$	
298.15	0.9974	0.921
308.15	0.9944	0.760
318.15	0.9906	0.635

[a] Molality of cetrimonium bromide in water in mol·kg^{-1}.

were taken to average the flow time. The viscosity of solution, η, is given by the following equation:

$$\eta = (Kt - L/t)\rho \tag{1}$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. The uncertainty in viscosity measurements is within ± 0.003 mPa·s.

Stock solutions of carbohydrates in different aqueous cetrimonium bromide solutions were prepared by mass (Mettler Toledo AG285 with uncertainty ± 0.0003 g), and the working solutions were prepared by mass. The experimental values of molality, densities, viscosities, apparent molar volume, and $(\eta_r - 1)/m^{1/2}$ at various temperatures are reported in Table 2.

Results and Discussion

The apparent molar volumes (ϕ_V) were determined from the solution densities using the following equation:[2]

$$\phi_V = M/\rho - 1000(\rho - \rho_0)/m\rho\rho_0 \tag{2}$$

where M is the molar mass of the solute, m is the molality of the solution, and ρ_0 and ρ are the densities of the solvent and the solution, respectively. As the plots of ϕ_V values against the square root of molality ($m^{1/2}$) were linear, ϕ_V values were fitted to the Masson equation:[3]

$$\phi_V = \phi_V^0 + S_V^*\sqrt{m} \tag{3}$$

where ϕ_V^0 is the limiting apparent molar volume at infinite dilution, S_V^* is the experimental slope, and m is the molality of the solution. The ϕ_V^0 values have been determined by fitting the dilute data ($m < 0.1$ mol·kg^{-1}) to eq 3 using a weighted least-squares fit.

The standard deviation (σ) were determined from ϕ_V^0 values using the following equation:

$$\sigma = \sqrt{\frac{\sum (Y_{exp} - Y_{cal})^2}{N - 1}} \tag{4}$$

where Y is the limiting apparent molar volume of the solution (ϕ_V^0) and N is the number of data points.

Values of ϕ_V^0 and S_V^* along with the corresponding standard deviation (σ) are listed in Table 3. A graphical representation of the limiting apparent molar volume of D-glucose, D-mannitol, and D-sucrose with different masses of cetrimonium bromide and different temperatures has been shown in Figures 1 to 3, respectively (also see Scheme 2). The estimated uncertainties in ϕ_V^0 are equal to the standard deviation (σ), the root-mean-square of the deviation between the experimental and the calculated ϕ_V^0 for each data point. A perusal of Table 3 reveals that the ϕ_V^0 values are positive and increase with the rise in temperature as well as the mass of cetrimonium bromide in the solvent mixture. This indicates the presence of strong solute−solvent interactions, and these interactions are strengthened with the rise in temperature and with an increase in the mass of cetrimonium bromide in the solvent mixture.

As is evident from the ϕ_V^0 values, the trend in the solute−solvent interaction of the carbohydrates is as follows: D-sucrose > D-mannitol > D-glucose (see Scheme 3).

The observed result can also be explained in view of the molar volume of the solvents and limiting apparent molar volume of the solute studied here reported in Table 4. The greater the difference in the volume, the greater is the fitness of the solute molecules in the solvent mixture rendering higher solute−solvent interaction. The same type of work has been done by the workers reported earlier.[4] The limiting apparent molar volume of the three carbohydrates is far greater than the molar volume of the cetrimonium bromide solution. The limiting apparent molar volume of the carbohydrates further increases with the temperature and the concentration of the cetrimonium bromide. Hence, the carbohydrate easily fits in the cetrimonium bromide solution resulting in more solute−solvent interaction between them which is an excellent agreement with the conclusion drawn from the values of ϕ_V^0 as well as the viscosity B-coefficient. The order of fitness, that is, solute−solvent interaction of the carbohydrate compound in the solvent mixture is given: D-sucrose > D-mannitol > D-glucose.

The parameter S_V^* is the volumetric virial coefficient that characterizes the pairwise interaction of solvated species in solution.[5−8] The sign of S_V^* is determined by the interaction between the solute species. In the present study S_V^* values were found to be negative and decrease further as the experimental temperature and mass of the cetrimonium bromide increases. This trend in S_V^* values indicates weak solute−solute interactions in the mixtures. A quantitative comparison of the magnitude of values shows that ϕ_V^0 values are much greater in magnitude than those of S_V^* for all of the solutions. This suggests that solute−solvent interactions dominate over solute−solute interactions in all of the solutions and at all experimental temperatures. Furthermore, S_V^* values are negative at all temperatures, and the values decrease with the increase of all experimental temperatures which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of solute−solute interactions. Again, the S_V^* values decrease with the increasing amount of cetrimonium bromide in the solvent mixture which may be attributed to the increase in the solvation of ions.

The variation of ϕ_V^0 with the temperature of the carbohydrates in solvent mixture follows the polynomial,

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \tag{5}$$

Table 2. Molalities (m), Densities (ρ), Viscosities (η), Apparent Molar Volumes (ϕ_V), and $(\eta_r - 1)/m^{1/2}$ for Carbohydrates in Different Molality (m_1) of Cetrimonium Bromide (1) + Water (2) Solutions at (298.15, 308.15, 318.15) K

m / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	η / mPa·s	$\phi_V \cdot 10^6$ / m^3·mol^{-1}	$(\eta_r - 1)/m^{1/2}$	m / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	η / mPa·s	$\phi_V \cdot 10^6$ / m^3·mol^{-1}	$(\eta_r - 1)/m^{1/2}$
		$m_1 = 0.001$					$m_1 = 0.001$		
		D-Glucose					D-Glucose		
		T/K = 298.15					T/K = 298.15		
0.0121	0.9979	0.907	121.55	0.085	0.0566	1.0006	0.928	120.32	0.140
0.0242	0.9986	0.913	121.07	0.106	0.0729	1.0016	0.936	119.99	0.153
0.0403	0.9996	0.921	120.61	0.127	0.0852	1.0023	0.942	119.70	0.165
		T/K = 308.15					T/K = 308.15		
0.0121	0.9949	0.751	123.75	0.082	0.0566	0.9975	0.769	122.13	0.141
0.0242	0.9956	0.756	123.15	0.100	0.0729	0.9985	0.775	121.70	0.154
0.0403	0.9965	0.762	122.52	0.122	0.0852	0.9992	0.780	121.35	0.164
		T/K = 318.15					T/K = 318.15		
0.0121	0.9911	0.622	125.00	0.073	0.0566	0.9937	0.637	122.42	0.136
0.0242	0.9918	0.626	124.08	0.097	0.0729	0.9947	0.642	121.83	0.153
0.0403	0.9927	0.631	123.18	0.118	0.0852	0.9954	0.646	121.47	0.161
		$m_1 = 0.001$					$m_1 = 0.001$		
		D-Mannitol					D-Mannitol		
		T/K = 298.15					T/K = 298.15		
0.0121	0.9979	0.907	122.98	0.089	0.0569	1.0007	0.930	120.48	0.146
0.0243	0.9987	0.913	122.01	0.106	0.0732	1.0017	0.937	119.88	0.159
0.0405	0.9997	0.922	121.12	0.128	0.0856	1.0025	0.943	119.37	0.170
		T/K = 308.15					T/K = 308.15		
0.0121	0.9949	0.751	125.43	0.079	0.0569	0.9976	0.770	122.34	0.143
0.0243	0.9956	0.756	124.32	0.104	0.0732	0.9986	0.776	121.55	0.156
0.0405	0.9966	0.763	123.40	0.124	0.0856	0.9994	0.781	121.00	0.167
		T/K = 308.15					T/K = 308.15		
0.0121	0.9911	0.621	129.15	0.070	0.0569	0.9937	0.636	124.13	0.134
0.0243	0.9917	0.626	127.40	0.095	0.0732	0.9948	0.642	122.85	0.150
0.0405	0.9927	0.631	125.65	0.118	0.0856	0.9956	0.646	121.95	0.162
		$m_1 = 0.001$					$m_1 = 0.001$		
		D-Sucrose					D-Sucrose		
		T/K = 298.15					T/K = 298.15		
0.0121	0.9986	0.903	224.68	0.041	0.0569	1.0041	0.928	219.01	0.139
0.0242	1.0001	0.909	222.61	0.074	0.0734	1.0062	0.937	217.82	0.160
0.0405	1.0021	0.918	220.61	0.107	0.0858	1.0078	0.946	217.21	0.179
		T/K = 308.15					T/K = 308.15		
0.0121	0.9956	0.747	225.85	0.032	0.0569	1.0011	0.769	219.64	0.137
0.0242	0.9971	0.752	223.56	0.071	0.0734	1.0032	0.777	218.20	0.160
0.0405	0.9991	0.760	221.40	0.107	0.0858	1.0048	0.783	217.29	0.180
		T/K = 318.15					T/K = 318.15		
0.0121	0.9918	0.619	227.69	0.029	0.0569	0.9973	0.636	219.94	0.133
0.0242	0.9933	0.623	224.80	0.064	0.0734	0.9994	0.643	218.20	0.160
0.0405	0.9953	0.630	222.13	0.103	0.0858	1.0010	0.649	217.13	0.179
		$m_1 = 0.003$					$m_1 = 0.003$		
		D-Glucose					D-Glucose		
		T/K = 298.15					T/K = 298.15		
0.0121	0.9980	0.919	121.83	0.084	0.0565	1.0007	0.941	120.32	0.140
0.0241	0.9987	0.925	121.25	0.102	0.0728	1.0017	0.948	119.99	0.153
0.0403	0.9997	0.933	120.73	0.123	0.0851	1.0024	0.953	119.70	0.162
		T/K = 308.15					T/K = 308.15		
0.0121	0.9950	0.759	124.20	0.080	0.0565	0.9976	0.778	122.13	0.141
0.0241	0.9957	0.765	123.49	0.104	0.0728	0.9986	0.784	121.64	0.156
0.0403	0.9966	0.771	122.73	0.124	0.0851	0.9993	0.789	121.30	0.167
		T/K = 318.15					T/K = 318.15		
0.0121	0.9912	0.627	125.84	0.073	0.0565	0.9938	0.642	122.49	0.138
0.0241	0.9919	0.631	124.47	0.098	0.0728	0.9948	0.648	121.83	0.153
0.0403	0.9928	0.637	123.46	0.120	0.0851	0.9955	0.652	121.29	0.163
		$m_1 = 0.003$					$m_1 = 0.003$		
		D-Mannitol					D-Mannitol		
		T/K = 298.15					T/K = 298.15		
0.0121	0.9980	0.918	123.52	0.078	0.0566	1.0008	0.940	120.52	0.137
0.0241	0.9987	0.924	122.41	0.100	0.0729	1.0018	0.948	119.89	0.152
0.0403	0.9997	0.932	121.37	0.121	0.0851	1.0026	0.953	119.39	0.162

Table 2. Continued

m / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	η / mPa·s	$\phi_V \cdot 10^6$ / m^3·mol^{-1}	$(\eta_r - 1)/m^{1/2}$	m / mol·kg^{-1}	$\rho \cdot 10^{-3}$ / kg·m^{-3}	η / mPa·s	$\phi_V \cdot 10^6$ / m^3·mol^{-1}	$(\eta_r - 1)/m^{1/2}$
		T/K = 308.15					T/K = 308.15		
0.0121	0.9950	0.759	126.40	0.080	0.0566	0.9977	0.778	122.34	0.142
0.0241	0.9957	0.764	124.87	0.099	0.0729	0.9987	0.784	121.20	0.158
0.0403	0.9967	0.771	123.56	0.125	0.0851	0.9995	0.789	120.71	0.169
		T/K = 318.15					T/K = 318.15		
0.0121	0.9911	0.627	129.66	0.073	0.0566	0.9938	0.643	124.14	0.140
0.0241	0.9918	0.632	127.91	0.101	0.0729	0.9948	0.648	123.06	0.156
0.0403	0.9928	0.637	125.93	0.121	0.0851	0.9956	0.653	122.20	0.172
		$m_1 = 0.003$					$m_1 = 0.003$		
		D-Sucrose					D-Sucrose		
		T/K = 298.15					T/K = 298.15		
0.0121	0.9987	0.914	226.15	0.040	0.0569	1.0042	0.940	219.30	0.137
0.0242	1.0002	0.921	223.81	0.072	0.0734	1.0063	0.950	217.77	0.162
0.0405	1.0022	0.931	221.28	0.111	0.0859	1.0079	0.958	216.67	0.179
		T/K = 308.15					T/K = 308.15		
0.0121	0.9957	0.755	226.55	0.028	0.0569	1.0012	0.776	219.60	0.133
0.0242	0.9972	0.760	223.85	0.066	0.0734	1.0033	0.785	217.82	0.159
0.0405	0.9992	0.767	221.53	0.099	0.0859	1.0049	0.792	216.95	0.178
		T/K = 318.15					T/K = 318.15		
0.0121	0.9919	0.624	228.53	0.026	0.0569	0.9974	0.642	220.34	0.135
0.0242	0.9933	0.628	225.35	0.065	0.0734	0.9995	0.649	218.75	0.166
0.0405	0.9953	0.635	222.97	0.106	0.0859	1.0011	0.655	217.60	0.181
		$m_1 = 0.005$					$m_1 = 0.005$		
		D-Glucose					D-Glucose		
		T/K = 298.15					T/K = 298.15		
0.0120	0.9981	0.929	121.89	0.082	0.0565	1.0008	0.951	120.42	0.138
0.0241	0.9988	0.936	121.34	0.102	0.0728	1.0018	0.959	120.01	0.153
0.0403	0.9998	0.944	120.81	0.122	0.0851	1.0025	0.965	119.71	0.164
		T/K = 308.15					T/K = 308.15		
0.0120	0.9951	0.766	124.68	0.076	0.0565	0.9977	0.785	122.28	0.139
0.0241	0.9958	0.772	123.81	0.100	0.0728	0.9986	0.792	121.75	0.153
0.0403	0.9967	0.779	122.98	0.122	0.0851	0.9994	0.797	121.38	0.166
		T/K = 318.15					T/K = 318.15		
0.0120	0.9913	0.640	126.40	0.071	0.0565	0.9938	0.656	123.12	0.138
0.0241	0.9919	0.644	125.28	0.096	0.0728	0.9948	0.661	122.17	0.153
0.0403	0.9929	0.650	124.04	0.119	0.0851	0.9956	0.665	121.66	0.163
		$m_1 = 0.005$					$m_1 = 0.005$		
		D-Mannitol					D-Mannitol		
		T/K = 298.15					T/K = 298.15		
0.0121	0.9981	0.929	126.38	0.073	0.0566	1.0008	0.950	121.48	0.133
0.0242	0.9988	0.935	124.58	0.096	0.0729	1.0019	0.958	120.27	0.150
0.0403	0.9998	0.943	122.80	0.117	0.0851	1.0027	0.965	119.31	0.162
		T/K = 308.15					T/K = 308.15		
0.0121	0.9950	0.766	129.50	0.071	0.0566	0.9977	0.785	123.29	0.135
0.0242	0.9957	0.771	127.16	0.094	0.0729	0.9988	0.791	122.03	0.150
0.0403	0.9967	0.778	125.05	0.115	0.0851	0.9996	0.796	120.95	0.161
		T/K = 318.15					T/K = 318.15		
0.0121	0.9912	0.640	130.92	0.071	0.0566	0.9939	0.656	124.45	0.140
0.0242	0.9919	0.645	128.48	0.100	0.0729	0.9949	0.662	122.85	0.158
0.0403	0.9929	0.650	126.21	0.121	0.0851	0.9957	0.667	121.95	0.172
		$m_1 = 0.005$					$m_1 = 0.005$		
		D-Sucrose					D-Sucrose		
		T/K = 298.15					T/K = 298.15		
0.0121	0.9988	0.924	227.51	0.029	0.0569	1.0045	0.950	219.96	0.131
0.0242	1.0003	0.931	224.95	0.069	0.0734	1.0067	0.960	218.29	0.156
0.0405	1.0023	0.940	222.06	0.101	0.0858	1.0084	0.968	217.20	0.174
		T/K = 308.15					T/K = 308.15		
0.0121	0.9958	0.762	228.44	0.026	0.0569	1.0015	0.784	220.67	0.131
0.0242	0.9974	0.767	225.33	0.062	0.0734	1.0037	0.793	218.68	0.159
0.0405	0.9994	0.775	222.66	0.099	0.0858	1.0054	0.799	217.33	0.178
		T/K = 318.15					T/K = 318.15		
0.0121	0.9920	0.636	229.40	0.021	0.0569	0.9977	0.655	221.71	0.135
0.0242	0.9935	0.641	226.60	0.063	0.0734	0.9999	0.663	219.60	0.163
0.0405	0.9956	0.648	224.00	0.103	0.0858	1.0015	0.669	218.40	0.182

Table 3. Limiting Apparent Molar Volumes (ϕ_V^0) and the Experimental Slopes (S_V^*) of Equation 3 for Carbohydrates along with the Standard Deviation (σ) in Different Molalities (m_1) of Cetrimonium Bromide (1) + Water (2) Solutions at (298.15, 308.15, and 318.15) K

	$\phi_V^0 \cdot 10^6$			$S_V^* \cdot 10^6$					
solvent mixture	$m^3 \cdot mol^{-1}$			$m^3 \cdot mol^{-3/2} \cdot L^{1/2}$			σ		
				D-Glucose					
T/K	298.15	308.15	318.15	298.15	308.15	318.15	298.15	308.15	318.15
$m_1 = 0.001$	122.62	125.16	127.12	−9.8705	−12.9438	−19.5447	0.0009	0.0007	0.0015
$m_1 = 0.003$	123.07	125.96	128.42	−11.5170	−16.0250	−24.6210	0.0000	0.0001	0.0012
$m_1 = 0.005$	123.19	126.65	129.33	−11.8484	−18.1721	−26.3000	0.0007	0.0006	0.0000
				D-Mannitol					
T/K	298.15	308.15	318.15	298.15	308.15	318.15	298.15	308.15	318.15
$m_1 = 0.001$	125.07	128.12	133.54	−19.3746	−24.2521	−39.4761	0.0005	0.0004	0.0007
$m_1 = 0.003$	125.95	129.84	134.27	−22.5825	−31.5661	−41.6590	0.0006	0.0035	0.0037
$m_1 = 0.005$	130.57	134.48	136.22	−38.4019	−46.5299	−49.3516	0.0012	0.0011	0.0084
				D-Sucrose					
T/K	298.15	308.15	318.15	298.15	308.15	318.15	298.15	308.15	318.15
$m_1 = 0.001$	229.04	230.90	233.88	−41.2324	−46.8402	−57.8321	0.0316	0.0068	0.0188
$m_1 = 0.003$	231.85	232.17	234.86	−52.0602	−52.5332	−59.5532	0.0035	0.0166	0.0195
$m_1 = 0.005$	233.70	234.82	236.03	−56.9237	−59.7467	−60.2582	0.0156	0.0001	0.0003

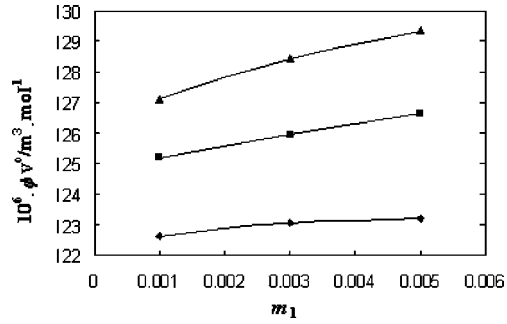


Figure 1. Plot of $10^6 \cdot \phi_V^0/m^3 \cdot mol^{-1}$ of D-glucose as a function of mass fraction of cetrimonium bromide in different binary mixtures of cetrimonium bromide (1) + water (2); —♦—, 298.15 K; —■—, 308.15 K; and —▲—, 318.15 K.

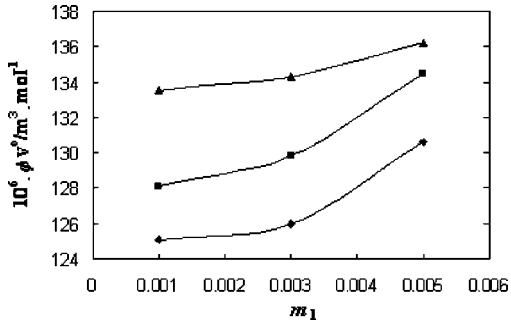


Figure 2. Plot of $10^6 \cdot \phi_V^0/m^3 \cdot mol^{-1}$ of D-mannitol as a function of mass fraction of cetrimonium bromide in different binary mixtures of cetrimonium bromide (1) + water (2); —♦—, 298.15 K; —■—, 308.15 K; and —▲—, 318.15 K.

over the temperature range under study where T is the temperature in K. a_0, a_1, and a_2 are the empirical constants depending on the solute and the solvents. The values of these coefficients of the above equation for the carbohydrates for aqueous cetrimonium bromide mixtures are reported in Table 5.

The limiting apparent molar expansibilities ϕ_E^0 can be obtained by the following equation:

$$\phi_E^0 = (\delta\phi_V^0/\delta T)_P = a_1 + 2a_2T \qquad (6)$$

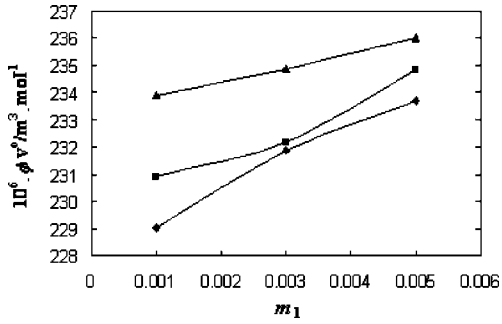
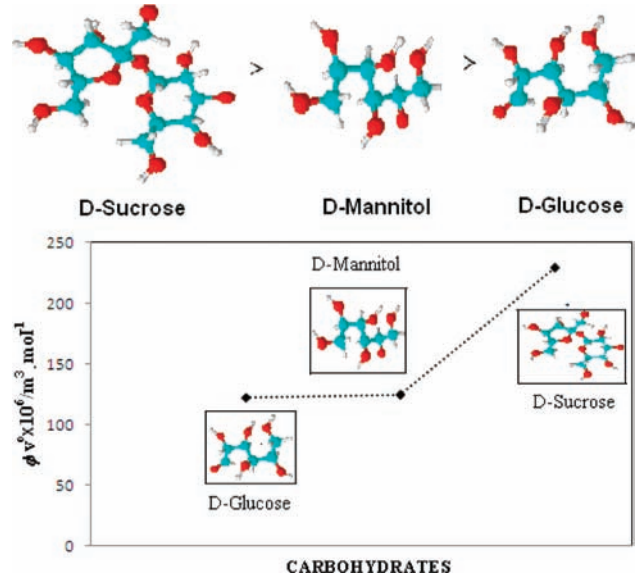


Figure 3. Plot of $10^6 \cdot \phi_V^0/m^3 \cdot mol^{-1}$ of D-sucrose as a function of mass fraction of cetrimonium bromide in different binary mixtures of cetrimonium bromide (1) + water (2); —♦—, 298.15 K; —■—, 308.15 K; and —▲—, 318.15 K.

Scheme 2



The values of ϕ_E^0 for different solutions of the studied carbohydrates at (298.15, 308.15, and 318.15) K are reported in Table 6. Table 6 reveals that ϕ_E^0 for D-glucose decreases with increasing temperature but increases for D-mannitol and D-sucrose. This fact can ascribed to the absence of caging or packing effect[9,10] in the mixed solutions of D-glucose. However,

Scheme 3. Order of Interaction Among the Molecules

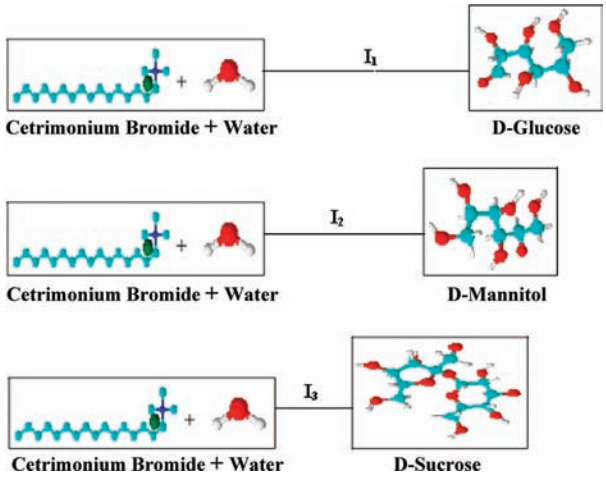


Table 4. Values of Molar Volume (V_m) and Limiting Apparent Molar Volume (ϕ_V) of Cetrimonium Bromide (1) + Water (2) Solution and Carbohydrates, Respectively, at 298.15 K

	V_m	$\phi_V^0 \cdot 10^6/m^3 \cdot mol^{-1}$		
solvent mixture	$m^3 \cdot mol^{-1}$	D-glucose	D-mannitol	D-sucrose
$m_1 = 0.001$	18.08	122.62	125.07	229.04
$m_1 = 0.003$	18.09	123.07	125.95	231.85
$m_1 = 0.005$	18.11	123.19	130.57	233.70

Table 5. Values of Various Coefficients (a_0, a_1, and a_2) of Equation 5 for Carbohydrates in Different Molality (m_1) of Cetrimonium Bromide (1) + Water (2) Solutions

	$a_0 \cdot 10^6$	$a_1 \cdot 10^6$	$a_2 \cdot 10^6$
solvent mixture	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1} \cdot K^{-1}$	$m^3 \cdot mol^{-1} \cdot K^{-2}$
	D-Glucose		
$m_1 = 0.001$	−222.21	2.030	−0.0029
$m_1 = 0.003$	−162.87	1.607	−0.0022
$m_1 = 0.005$	−334.73	2.688	−0.0039
	D-Mannitol		
$m_1 = 0.001$	1119.70	−6.859	0.0118
$m_1 = 0.003$	258.26	−1.250	0.0027
$m_1 = 0.005$	−980.95	6.957	−0.0108
	D-Sucrose		
$m_1 = 0.001$	690.68	−3.226	0.0056
$m_1 = 0.003$	1311.90	−7.158	0.0119
$m_1 = 0.005$	240.58	−0.154	0.0004

for values of ϕ_E^0 with the increase in the cetrimonium bromide in the solvent mixture were found to be rather complicated to explain.

During the past few years it has been emphasized by different workers that S_V^* is not the sole criterion for determining the structure-making or -breaking nature of any solute. Hepler[11] developed a technique of examining the sign of $(\delta\phi_E^0/\delta T)_P$ for the solute in terms of long-range structure-making and -breaking capacity of the solute in the mixed solvent systems using the general thermodynamic expression,

$$(\delta\phi_E^0/\delta T)_P = (\delta^2\phi_V^0/\delta T^2)_P = 2a_2 \qquad (7)$$

If the sign of $(\delta\phi_E^0/\delta T)_P$ is negative or a small positive, the molecule is a structure breaker; otherwise, it is a structure maker.[12] As is evident from Table 6, the carbohydrates under investigation are predominantly structure breakers in all of the experimental solutions.

Table 6. Limiting Apparent Molar Expansibilities (ϕ_E^0) for Carbohydrates in Different Molality (m_1) of Cetrimonium Bromide (1) + Water (2) Solutions at (298.15, 308.15, and 318.15) K

	$\phi_E^0 \cdot 10^6$			$(\delta\phi_E^0/\delta T)_p \cdot 10^6$
solvent mixture	$m^3 \cdot mol^{-1} \cdot K^{-1}$			$m^3 \cdot mol^{-1} \cdot K^{-2}$
	D-Glucose			
T/K	298.15	308.15	318.15	
$M_1 = 0.001$	0.3004	0.2424	0.1844	−0.0058
$M_1 = 0.003$	0.2949	0.2509	0.2069	−0.0044
$M_1 = 0.005$	0.3623	0.2843	0.2063	−0.0078
	D-Mannitol			
T/K	298.15	308.15	318.15	
$M_1 = 0.001$	0.1771	0.4131	0.6491	0.0236
$M_1 = 0.003$	0.3603	0.4143	0.4683	0.0054
$M_1 = 0.005$	0.5170	0.3010	0.0850	−0.0216
	D-Sucrose			
T/K	298.15	308.15	318.15	
$m_1 = 0.001$	0.1131	0.2251	0.3371	0.0112
$m_1 = 0.003$	−0.0624	0.1756	0.4136	0.0238
$m_1 = 0.005$	0.0847	0.0927	0.1007	0.0008

The viscosity data of the experimental solutions of carbohydrates have been analyzed using the Jones−Dole equation,[13]

$$(\eta/\eta_0 - 1)/\sqrt{m} = (\eta_r - 1)/\sqrt{m} = A + B\sqrt{m} \qquad (8)$$

where the relative viscosity $\eta_r = \eta/\eta_0$, η_0 and η are the viscosities of the solvent and solution, respectively, and m is the molality of a solution. A and B are the Jones−Dole[13] constants estimated by a least-squares method and reported in Table 7. The values of the A coefficient are found to decrease with temperature and decrease with the increase in mass of cetrimonium bromide in the solvent mixture. These results indicate the presence of very weak solute−solute interactions, and these interactions further decrease with the rise of experimental temperatures and decrease with an increase in mass cetrimonium bromide in solvent mixture. These results are in excellent agreement with those obtained from S_V^* values.

The viscosity B-coefficient[14,15] reflects the effects of solute−solvent interactions on the solution viscosity. The viscosity B-coefficient is a valuable tool to provide information concerning the solvation of solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules. From Table 7 it is evident that the values of the B-coefficient of carbohydrates in the studied solvent systems suggest the presence of strong solute−solvent interactions, and these type of interactions are strengthened with a rise in temperature and also increase with an increase of cetrimonium bromide in the solvent mixtures. These conclusions are in excellent agreement with those drawn from ϕ_V^0 values discussed earlier.

It has been reported in a number of studies[16,17] that dB/dT is a better criterion for determining the structure-making/breaking nature of any solute rather than simply the value of the B-coefficient. It is found from Table 7 that the values of the B-coefficient increase with a rise in temperature (positive dB/dT), suggesting the structure-breaking tendency of carbohyrates in the solvent systems.

The viscosity data have also been analyzed on the basis of transition state theory for the relative viscosity of the solutions as suggested by Feakins et al.[18] using the relation,

Table 7. Values of Viscosity *A* and *B* Coefficients Derived from Equation 8 for Carbohydrates in Different Molalities (m_1) of Cetrimonium Bromide (1) + Water (2) Solutions at (298.15, 308.15, and 318.15) K

	B			*A*		
solvent mixture	$L \cdot mol^{-1}$			$L^{1/2} \cdot mol^{-1/2}$		
			D-Glucose			
T/K	298.15	308.15	318.15	298.15	308.15	318.15
$m_1 = 0.001$	0.423 ± 0.010	0.456 ± 0.008	0.486 ± 0.007	0.040 ± 0.002	0.031 ± 0.002	0.021 ± 0.002
$m_1 = 0.003$	0.433 ± 0.005	0.471 ± 0.006	0.492 ± 0.008	0.036 ± 0.001	0.029 ± 0.001	0.020 ± 0.002
$m_1 = 0.005$	0.448 ± 0.005	0.485 ± 0.008	0.506 ± 0.007	0.031 ± 0.001	0.024 ± 0.002	0.017 ± 0.002
			D-Mannitol			
T/K	298.15	308.15	318.15	298.15	308.15	318.15
$m_1 = 0.001$	0.449 ± 0.009	0.476 ± 0.009	0.494 ± 0.008	0.038 ± 0.002	0.028 ± 0.002	0.017 ± 0.002
$m_1 = 0.003$	0.459 ± 0.004	0.495 ± 0.009	0.527 ± 0.016	0.028 ± 0.001	0.024 ± 0.002	0.016 ± 0.003
$m_1 = 0.005$	0.482 ± 0.008	0.499 ± 0.004	0.540 ± 0.013	0.020 ± 0.002	0.016 ± 0.001	0.013 ± 0.003
			D-Sucrose			
T/K	298.15	308.15	318.15	298.15	308.15	318.15
$m_1 = 0.001$	0.754 ± 0.011	0.799 ± 0.009	0.822 ± 0.006	−0.043 ± 0.002	−0.055 ± 0.002	−0.063 ± 0.002
$m_1 = 0.003$	0.770 ± 0.010	0.817 ± 0.011	0.854 ± 0.011	−0.046 ± 0.002	−0.062 ± 0.002	−0.067 ± 0.002
$m_1 = 0.005$	0.782 ± 0.010	0.832 ± 0.008	0.876 ± 0.006	−0.055 ± 0.002	−0.067 ± 0.002	−0.074 ± 0.001

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + RT(1000B + \phi_2^0 - \phi_1^0)/\phi_1^0 \qquad (9)$$

where ϕ_1^0 and ϕ_2^0 are the limiting apparent molar volumes of the solvent and solute, respectively. The contribution per mole of the solute to the free energy of activation of viscous flow, $\Delta\mu_2^{0\neq}$, of the solutions was determined from the above relation and is listed in Table 9 (given as Supporting Information). The free energy of activation of viscous flow for the solvent mixture, $\Delta\mu_1^{0\neq}$, is given by the relation:

$$\Delta\mu_1^{0\neq} = \Delta G_1^{0\neq} = RT \ln(\eta_0\phi_1^0/hN_A) \qquad (10)$$

where N_A is the Avogadro's number, $\Delta G_1^{0\neq}$ is the Gibb's free energy of viscous flow, η_0 is the viscosity of the solvent mixture, ϕ_1^0 is the limiting apparent molar volume of the solvent, and *h* is the Plank's constant. The values of the parameters $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ are reported in Tables 8 and 9, respectively (given as Supporting Information).

The entropy of activation for electrolytic solutions has been calculated using the relation:[18,19]

$$\Delta S_2^{0\neq} = -\mathrm{d}(\Delta\mu_2^{0\neq})/\mathrm{d}T \qquad (11)$$

where $\Delta S_2^{0\neq}$ has been obtained from the negative slope of the plots of $\Delta\mu_2^{0\neq}$ against *T* by using a least-squares treatment.

The activation enthalpy ($\Delta H_2^{0\neq}$) has been calculated using the relation:[18,19]

$$\Delta H_2^{0\neq} = \Delta\mu_2^{0\neq} + T\Delta S_2^{0\neq} \qquad (12)$$

The value of $\Delta S_2^{0\neq}$ and $\Delta H_2^{0\neq}$ are listed in Table 9 (given as Supporting Information).

Conclusion

In summary, ϕ_V^0 and viscosity *B*-coefficient values for carbohydrates indicate the presence of strong solute−solvent interactions, and these interactions are further strengthened at higher temperatures and higher concentrations of cetrimonium bromide in the solvent mixture. In the case of D-mannitol the solute−solvent interaction is higher than the D-glucose with a higher temperature and higher concentration of the cetrimonium bromide in the solvent mixture, but in the case of D-sucrose the solute−solvent interaction is nearly double than that of the D-glucose and D-mannitol. Also, the carbohydrates under study were found to act as a structure breaker in the solvent mixtures studied.

Supporting Information Available:

Supplementary Tables 8 and 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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