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SHORT ARTICLE

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Volumetric and Transport Behavior of Different Carbohydrates in Aqueous and Aqueous Urea Mixtures at Different Temperatures

Sudhakar S. Dhondge*

P. G. Department of Chemistry, S. K. Porwal College, Kamptee, Dist. Nagpur-441 002, India

Chandrashekhar P. Pandhurnekar

Department of Applied Chemistry, Shri Ramdeobaba Kamla Nehru Engineering College, Nagpur-440 013, India

Sunil Garade and Kanhaiya Dadure

Department of Chemistry, R. T. M. Nagpur University, Nagpur-440 033, India

S *Supporting Information*

ABSTRACT: Densities and viscosities of aqueous solutions and 1.0 mol·kg^{-1} aqueous urea solutions of glucose, fructose, sucrose, and lactose have been measured at two different temperatures [(308.15 and 318.15) K] in the concentration range (0 to 3) mol·kg^{-1}. The different derived parameters such as the apparent molal volume of solute (ϕ_V) and Jones–Dole equation viscosity *B*- and *D*-coefficients have been obtained for these binary and ternary mixtures. Partial molal volumes ($\overline{V}_2^0$) at infinite dilution were obtained by smooth extrapolation of the ϕ_V–m curves to zero concentration. These data were used to obtain the corresponding volume of transfer ($\Delta_{\text{trans}}\overline{V}_2^0$) for saccharides from pure water to 1.0 mol·kg^{-1} aqueous urea solutions at two different temperatures. The results are interpreted in terms of various interactions among solute and solvent molecules.

1. INTRODUCTION

A thermodynamic study of aqueous solutions of nonelectrolytes plays an important role in understanding the nature and extent of solute–solvent and solute–solute interactions.[1–3] Moreover, the study of carbohydrates/saccharides has become a subject of increasing interest because of the multidimensional physical, biochemical, and industrially useful properties of these compounds. In addition to their importance in the food, pharmaceutical, and chemical industries, simple saccharides have received considerable attention for their ability to protect biological macromolecules.[4–10] It is well-known that different polar groups such as hydroxyl groups can readily form H-bonds with highly polar water molecules. The hydration of a simple carbohydrate molecule is an essential model for understanding interactions between hydrophilic groups and interfacial water molecules.[11]

Several attempts have been made to gain a more fundamental insight into the molecular details of sugar solvation. Water is of the greatest interest, because of its ubiquity and biological and technological importance. The main features that set water apart from other liquids are its spatial and orientational intermolecular correlations, which are dominated by labile hydrogen-bond interactions, and its time-averaged tetrahedral geometry. Carbohydrates contain the –OH group and are able to interact with water. Configurationally, the situation is complex because the mutual spacing and orientation of the –OH vectors in different solute molecules can match those in water to varying degrees and such hydration disturbances are likely to be of a short-range nature.[12] Kabayama and Patterson first drew attention to the spatial compatibility of the –OH topology in water with that of equatorial –OH groups on pyranose sugars.[13] In the sugar molecule, the spacing of oxygen atoms linked to next-nearest carbon neighbors are of the order of 0.485 nm which is also the distance between next-nearest neighbor oxygen atoms in liquid water.[14]

Urea is one of the simplest molecules of biological interest. The structural features of the molecule in the gas phase[15] as well as the solid state[16] are largely known. The structure of aqueous urea solution continues to attract research interest due to some intriguing properties of concentrated aqueous urea solutions.[17] Urea increases the solubility of many hydrocarbon gases in water,[18] affects the stability of proteins,[19,20] and inhibits micelle formation. Most recently the structure of the urea–water system has been investigated through molecular dynamics simulations and analysis of Raman spectral band shapes.[21,22] It was concluded that urea molecules are solvated by water through several hydrogen bonding sites and the radial distribution of urea molecules in the solution is almost uniform.

Thus, it was thought worthwhile to investigate the effect of urea, a known protein denaturant, on the volumetric and viscometric behavior of the aqueous carbohydrates solutions. In the present communication, we report herewith the experimental data of densities and viscosities of different carbohydrates such as glucose, fructose, sucrose, and lactose in aqueous solution and in 1.0 mol·kg^{-1} aqueous urea solution at different temperatures (308.15 and 318.15 K) within the (0 to 3) mol·kg^{-1}

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Table 1. Density (ρ), Apparent Molal Volume of Solute (ϕ_V), Absolute Viscosity (η), and Relative Viscosity (η_r) of Carbohydrate in Water and Carbohydrate in (Urea + Water) Solutions at T = 308.15 K

m	$10^{-3}\,\rho$	$10^{6}\,\phi_V$	$10^{3}\,\eta$	
$\text{mol}\cdot\text{kg}^{-1}$	$\text{kg}\cdot\text{m}^{-3}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{N}\cdot\text{s}\cdot\text{m}^{-2}$	η_r
Glucose + Water				
0.0000	0.9940		0.719	1.000
0.5031	1.0261	113.08 ± 0.21	0.911	1.267
0.8113	1.0441	113.05 ± 0.13	1.037	1.442
1.0116	1.0551	113.24 ± 0.10	1.134	1.577
1.3130	1.0712	113.00 ± 0.08	1.278	1.778
1.7115	1.0900	113.53 ± 0.06	1.442	2.005
2.0184	1.1042	113.41 ± 0.06	1.711	2.379
3.0464	1.1445	114.00 ± 0.04	2.579	3.587
3.4868	1.1587	114.50 ± 0.03	3.084	4.289
Fructose + Water				
0.0000	0.9940		0.719	1.000
0.4062	1.0206	111.97 ± 0.25	0.863	1.200
0.6071	1.0329	111.99 ± 0.17	0.928	1.291
0.8084	1.0446	112.20 ± 0.13	1.010	1.405
1.2073	1.0666	112.24 ± 0.09	1.189	1.654
1.4124	1.0772	112.29 ± 0.08	1.305	1.815
1.6113	1.0866	112.60 ± 0.07	1.394	1.939
2.3255	1.1190	112.69 ± 0.05	1.833	2.550
2.5243	1.1275	112.61 ± 0.05	1.998	2.779
2.9823	1.1452	112.79 ± 0.04	2.372	3.299
Sucrose + Water				
0.0000	0.9940		0.719	1.000
0.1009	1.0069	213.01 ± 1.01	0.712	0.990
0.2018	1.0190	213.65 ± 0.51	0.777	1.081
0.4033	1.0419	213.89 ± 0.26	0.915	1.273
0.8044	1.0828	213.59 ± 0.14	1.291	1.795
1.0063	1.1011	213.64 ± 0.11	1.535	2.135
1.5930	1.1482	213.30 ± 0.07	2.588	3.600
2.0370	1.1756	214.91 ± 0.06	3.655	5.083
3.0246	1.2289	214.96 ± 0.04	6.396	8.896
Lactose + Water				
0.0000	0.9940		0.719	1.000
0.1004	1.0068	212.22 ± 1.02	0.784	1.091
0.2052	1.0198	211.51 ± 0.50	0.864	1.202
0.3032	1.0313	211.66 ± 0.34	0.934	1.299
0.3529	1.0371	211.32 ± 0.30	0.966	1.343
0.4036	1.0428	211.32 ± 0.26	1.012	1.408
0.4532	1.0479	212.16 ± 0.23	1.063	1.478
0.6061	1.0640	212.17 ± 0.18		
Glucose + 1.0 m Aqueous Urea Solution				
0.0000	1.0091		0.650	1.000
0.9133	1.0634	114.00 ± 0.11	0.972	1.495
1.0154	1.0688	114.10 ± 0.10	1.015	1.562
1.3208	1.0842	114.25 ± 0.08	1.158	1.782
1.8207	1.1074	114.41 ± 0.06	1.449	2.229
2.3424	1.1295	114.44 ± 0.05	1.805	2.777
2.6339	1.1405	114.64 ± 0.04	2.018	3.105
3.0415	1.1555	114.63 ± 0.04	2.388	3.674
Fructose + 1.0 m Aqueous Urea Solution				
0.0000	1.0091		0.650	1.000
0.2038	1.0223	113.35 ± 0.49	0.705	1.085
0.4066	1.0352	112.61 ± 0.25	0.773	1.189
0.6097	1.0469	113.42 ± 0.17	0.837	1.288
0.8119	1.0588	112.85 ± 0.13	0.912	1.402
1.2071	1.0800	112.90 ± 0.09	1.073	1.651
1.6206	1.1003	113.04 ± 0.07	1.270	1.954
2.3349	1.1315	113.32 ± 0.05	1.616	2.487
2.5285	1.1392	113.41 ± 0.04	1.835	2.823
3.0335	1.1587	113.32 ± 0.04	2.240	3.445
Sucrose + 1.0 m Aqueous Urea Solution				
0.0000	1.0091		0.650	1.000
0.1968	1.0326	216.88 ± 0.51	0.770	1.184
0.3958	1.0552	214.97 ± 0.26	0.915	1.407
0.5926	1.0756	214.93 ± 0.18	1.084	1.667
0.7885	1.0945	214.76 ± 0.13	1.303	2.004
0.9890	1.1122	214.93 ± 0.11	1.477	2.272
1.1790	1.1277	215.16 ± 0.09	1.819	2.799
1.5843	1.1572	218.23 ± 0.08	2.608	4.013
1.8250	1.1717	215.76 ± 0.07	3.191	4.909
Lactose + 1.0 m Aqueous Urea Solution				
0.0000	1.0091		0.650	1.000
0.1490	1.0264	221.65 ± 0.67	0.744	1.144
0.1963	1.0321	219.14 ± 0.51	0.773	1.189
0.2445	1.0374	219.59 ± 0.41	0.814	1.252
0.3461	1.0482	219.86 ± 0.29	0.876	1.347
0.4000	1.0532	221.29 ± 0.26	0.915	1.408
0.4449	1.0582	220.23 ± 0.23	0.961	1.478
0.5932	1.0732	219.25 ± 0.18		
0.6411	1.0777	219.30 ± 0.16		

concentration range. The different derived parameters such as the apparent molal volume (ϕ_V) of the solute and the Jones–Dole equation viscosity *B*-coefficients were obtained for these binary and ternary mixtures. The limiting apparent molal volumes of solutes (ϕ_V^0) were also obtained for aqueous binary mixtures by smooth extrapolation of the ϕ_V–m curves to zero concentration. The results are interpreted in terms of various interactions among solute and solvent molecules.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The chemicals used in the present work, that is, glucose (mass fraction purity >0.999), fructose (mass fraction purity >0.999), sucrose (mass fraction purity >0.999), lactose (mass fraction purity >0.999), and urea (mass fraction purity >0.995), were procured from E-Merck, India, and sodium chloride (mass fraction purity >0.999) was procured from Glaxo, India, and all of them were of A. R. (analytical reagent) grade. All of the carbohydrates were dried in vacuum oven at 333.15 K and sodium chloride at 423.15 K in the oven for 12 h. Then these

Table 2. Density (ρ), Apparent Molal Volume of Solute (ϕ_V), Absolute Viscosity (η), and Relative Viscosity (η_r) of Carbohydrate in Water and Carbohydrate in (Urea + Water) Solution at T = 318.15 K

m mol·kg^{-1}	$10^{-3}\,\rho$ kg·m^{-3}	$10^6\,\phi_V$ m^3·mol^{-1}	$10^3\,\eta$ N·s·m^{-2}	η_r
Glucose + Water				
0.0000	0.9902		0.597	1.000
0.5031	1.0224	113.11 ± 0.21	0.756	1.267
0.8113	1.0403	113.25 ± 0.13	0.861	1.442
1.0116	1.0513	113.38 ± 0.11	0.941	1.577
1.3130	1.0669	113.57 ± 0.08	1.061	1.778
1.7115	1.0860	113.82 ± 0.06	1.197	2.005
2.0184	1.0998	113.98 ± 0.06	1.420	2.379
3.0464	1.1404	114.32 ± 0.04	2.141	3.587
3.4868	1.1554	114.53 ± 0.03	2.561	4.289
Fructose + Water				
0.0000	0.9902		0.597	1.000
0.4057	1.0167	112.34 ± 0.26	0.696	1.166
0.6081	1.0289	112.69 ± 0.17	0.758	1.270
1.2165	1.0625	113.10 ± 0.09	0.946	1.585
1.4080	1.0714	113.80 ± 0.08	1.021	1.710
2.2998	1.1130	113.45 ± 0.05	1.469	2.461
3.5322	1.1585	113.98 ± 0.03	2.055	3.442
Sucrose + Water				
0.0000	0.9902		0.597	1.000
0.4037	1.0384	213.62 ± 0.26	0.771	1.292
0.6046	1.0591	214.51 ± 0.18	0.900	1.508
0.8065	1.0791	214.00 ± 0.14	0.984	1.648
1.0088	1.0972	214.37 ± 0.11	1.164	1.950
1.2072	1.1135	214.77 ± 0.09	1.431	2.397
2.0145	1.1706	215.17 ± 0.06	2.618	4.386
Lactose + Water				
0.0000	0.9902		0.597	1.000
0.1002	1.0027	215.41 ± 1.03	0.601	1.007
0.1519	1.0087	217.20 ± 0.68	0.621	1.041
0.2013	1.0143	218.11 ± 0.52	0.642	1.076
0.2521	1.0206	216.31 ± 0.41	0.670	1.122
0.3518	1.0311	218.19 ± 0.30	0.725	1.214
0.4053	1.0367	218.54 ± 0.26	0.757	1.268
0.6026	1.0567	218.46 ± 0.18	0.885	1.483
Glucose + 1.0 m Aqueous Urea Solution				
0.0000	1.0050		0.533	1.000
0.8901	1.0577	114.53 ± 0.12	0.774	1.452
1.0230	1.0648	114.56 ± 0.10	0.818	1.534
1.2798	1.0777	114.72 ± 0.08	0.916	1.718
2.2752	1.1220	114.95 ± 0.05	1.415	2.654
2.9544	1.1485	114.78 ± 0.04	1.763	3.309
Fructose + 1.0 m Aqueous Urea Solution				
0.0000	1.0050		0.533	1.000
0.4070	1.0309	113.34 ± 0.25	0.625	1.172
0.6118	1.0429	113.63 ± 0.17	0.675	1.266
0.8123	1.0543	113.60 ± 0.13	0.735	1.378
1.2149	1.0763	113.10 ± 0.09	0.862	1.617
1.4075	1.0852	113.70 ± 0.08	0.925	1.735
1.6182	1.0953	113.75 ± 0.07	1.004	1.884
2.3212	1.1257	114.08 ± 0.05	1.323	2.482
2.5389	1.1342	114.18 ± 0.04	1.474	2.765
Sucrose + 1.0 m Aqueous Urea Solution				
0.0000	1.0050		0.533	1.000
0.3952	1.0509	215.75 ± 0.26	0.699	1.311
0.5967	1.0712	216.45 ± 0.18	0.810	1.519
0.8013	1.0911	215.73 ± 0.13	0.972	1.824
1.1951	1.1244	215.96 ± 0.09	1.319	2.475
1.5800	1.1525	216.38 ± 0.07	1.965	3.686
1.9805	1.1787	216.36 ± 0.06	2.500	4.690
Lactose + 1.0 m Aqueous Urea Solution				
0.0000	1.0050		0.533	1.000
0.1971	1.0280	219.56 ± 0.51	0.583	1.094
0.2481	1.0336	219.95 ± 0.41	0.609	1.142
0.2966	1.0388	220.32 ± 0.34	0.634	1.190
0.3460	1.0440	220.41 ± 0.30	0.660	1.239
0.4445	1.0547	218.85 ± 0.23	0.725	1.361
0.5928	1.0687	220.23 ± 0.18	0.822	1.543
0.6415	1.0731	220.43 ± 0.17	0.857	1.608

were kept over anhydrous-fused calcium chloride in vacuum desiccators for more than two days. The water used for the sample preparation was freshly prepared doubly distilled water. All of the solutions were prepared on the molality basis by using analytical balance (E. Mettler) with an uncertainty in weight up to ± 0.1 mg. For binary solutions of carbohydrates, water has been used as solvent. In case of ternary solutions of carbohydrates, urea + water has been used as the solvent. For this purpose a stock solution of urea in water (1.0 m, i.e., 1.0 mol of urea is dissolved in 1 kg of water) was prepared and used as a solvent. Thus the molality for ternary solutions is the moles of carbohydrate dissolved per kilogram of (urea + water). In binary as well as ternary solutions the carbohydrate is used as the solute.

2.2. Methods. The densities of the all binary and ternary solutions were measured by using Lypkin's modified bicapillary pycnometers (volume ≈ 22 cm^3). The details are given elsewhere.[23] The viscosities of the solutions were measured using an Ostwald viscometer. Both the pycnometers and viscometer were immersed in an experimental water bath (capacity ≈ 40 L). The temperature in an experimental bath was maintained constant (± 0.01 K) by circulating the thermostatted liquid from U-10 Thermostat (MLW Mechanik Prüfgeräte Medingen, Germany) which maintains the temperature constant to ± 0.1 K inside the water bath of thermostat. The flow time measurements for aqueous and aqueous urea solutions of carbohydrates were made in triplicate. The average of the flow time was used to calculate the viscosity of the solution. The measurement of flow times were made with a "ROCAR" stop watch having an uncertainty of ± 0.1 s. The pycnometer and viscometer were calibrated by using aqueous NaCI solutions of different concentrations at (308.15 and 318.15) K. The

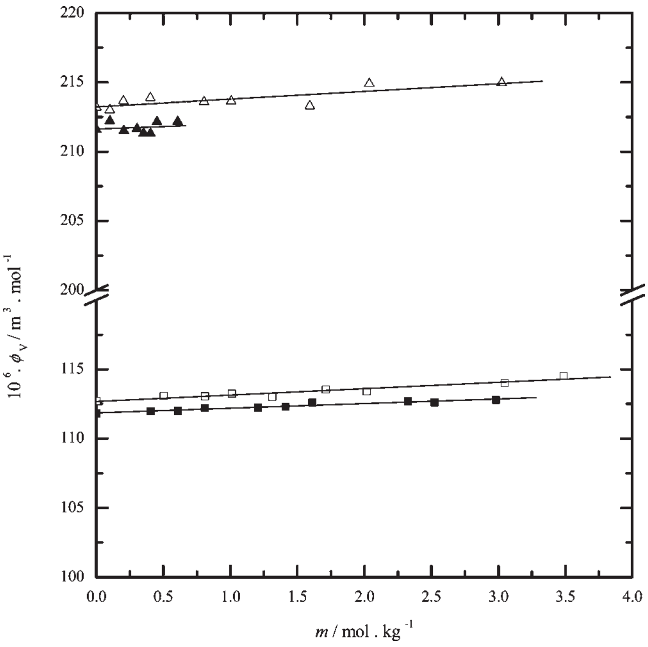

Figure 1. Plot of variation of the apparent molal volume of solute (ϕ_V) against the molality of solute (m) in aqueous solution at 308.15 K. □—□, glucose + water; ■—■, fructose + water; △—△, sucrose + water; ▲—▲, lactose + water.

experimental uncertainty[24] in the measurement of density was found to be ± 0.1 kg·m^{-3}. The uncertainty in the viscosity[25] measurements was of the order of ± 2 %.

3. CALCULATION OF DERIVED PARAMETERS

Apparent molal volumes (ϕ_V) of different carbohydrates in aqueous binary and aqueous urea ternary solutions at different temperatures have been calculated from the experimental values of densities using the following equation:

$$\phi_V = \left[\frac{1000(\rho_0 - \rho)}{m\rho\rho_0}\right] + \frac{M}{\rho} \tag{1}$$

where M is the molar mass of the solute, that is, carbohydrate, m is the molality of the solution, and ρ and ρ_0 are the densities of solution and pure water or 1.0 mol·kg^{-1} aqueous urea solution, respectively.

The limiting apparent molal volumes of solute (ϕ_V^0) or limiting partial molar volume of the solute ($\overline{V}_2^0$) were evaluated by smooth extrapolation of apparent molal volume (ϕ_V) of solute to the zero concentration using the least-squares fitting method. The values of the slope (S_V) of the ϕ_V−m curves were obtained by using the relation:

$$\phi_V = \phi_V^0 + S_V m \tag{2}$$

We are aware of the fact that our values of ϕ_V^0 cannot be that accurate as they have been extrapolated from higher concentrations (lowest concentration for particular system) but still are useful to interpret the results. The partial molal volumes of transfer ($\Delta_{\text{trans}}\overline{V}_2^0$) at infinite dilution from water to aqueous urea solution were calculated with the equation:

$$\Delta_{\text{trans}}\overline{V}_2^0 = \overline{V}_2^0(\text{in } 1.0\ m \text{ aqueous urea solution}) - \overline{V}_2^0(\text{in aqueous solution}) \tag{3}$$

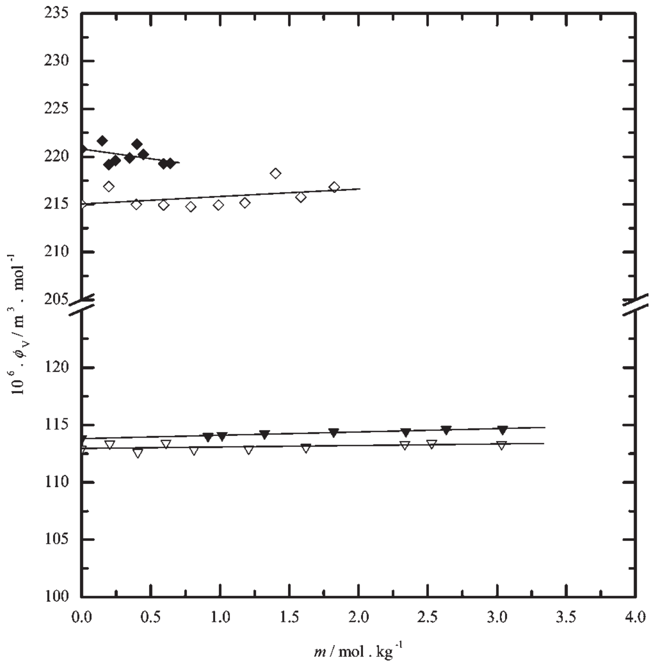

Figure 2. Plot of variation of the apparent molal volume of solute (ϕ_V) against the molality of solute (m) in aqueous solution at 308.15 K. ▼—▼, glucose + 1.0 m aqueous urea solution; ▽—▽, fructose + 1.0 m aqueous urea solution; ◇—◇, sucrose + 1.0 m aqueous urea solution; ◆—◆, lactose + 1.0 m aqueous urea solution.

The values of the limiting apparent molal expansivity were also obtained by using the relation:

$$\phi_E^0 = \frac{d\phi_V^0}{dT} \tag{4}$$

The relative viscosity (η_r) of binary and ternary mixtures was computed using a relation:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0} \tag{5}$$

where η, ρ, and t are the viscosity, density, and flow time for the solution, respectively, whereas η_0, ρ_o, and t_0 are the viscosity, density, and flow time for water or 1.0 m aqueous urea solvents, respectively.

From the plot of relative viscosity (η_r) against molality (m), the coefficients of viscosity (B- and D- coefficient) were obtained using an expression:

$$\frac{\eta}{\eta_0} = \eta_r = 1 + Bc + Dc^2 \tag{6}$$

where η, η_0, η_r, and c are the viscosity of solution, viscosity of solvents (water or 1 m aqueous urea), relative viscosity of solution, and molarity of the solution, respectively, and B and D are empirical coefficients known as the Jones−Dole viscosity coefficients of the systems. Also, the temperature derivative of the Jones−Dole viscosity B-coefficient, that is, dB/dT, has been calculated for all of the systems studied in the present work.

4. RESULTS AND DISCUSSION

In Table 1 the experimental values of density (ρ) and apparent molal volume of solute (ϕ_V) of different carbohydrates in aqueous and 1.0 m aqueous urea solution at 308.15 K are listed.

Table 3. Apparent Molal Volume of Solutes at Infinite Dilution (ϕ_V^0), Values of Slope (S_V), and the Limiting Apparent Molal Expansivity (ϕ_E^0) for Different Carbohydrates in Aqueous and 1.0 *m* Aqueous Urea Solution

	T/K = 308.15		T/K = 318.15		T/K = 313.15
	$10^6\ \phi_V^0$	$10^6\ S_V$	$10^6\ \phi_V^0$	$10^6\ S_V$	$10^6\ \phi_E^0$
system	$m^3 \cdot mol^{-1}$	$m^3 \cdot kg \cdot mol^{-2}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot kg \cdot mol^{-2}$	$m^3 \cdot mol^{-1} \cdot K^{-1}$
glucose + water	112.7	0.292	112.9	0.475	0.02
fructose + water	111.8	0.321	112.5	0.461	0.07
sucrose + water	213.2	0.548	213.5	0.840	0.03
lactose + water	211.6	0.291	215.9	4.979	0.43
glucose + 1.0 *m* aqueous urea solution	113.8	0.289	114.4	0.148	0.06
fructose + 1.0 *m* aqueous urea solution	112.9	0.123	113.1	0.355	0.02
sucrose + 1.0 *m* aqueous urea solution	215.0	0.772	215.7	0.289	0.07
lactose + 1.0 *m* aqueous urea solution	220.8	−2.068	219.6	0.777	−0.12

Table 4. Volume of Transfer ($\Delta_{trans}\overline{V}_2^0$) of Different Carbohydrates from an Aqueous Binary Mixture to 1.0 *m* Aqueous Urea Solution at Different Temperatures

	$(10^6\ \Delta_{trans}\overline{V}_2^0)/(m^3 \cdot mol^{-1})$	
compound	T/K = 308.15	T/K = 318.15
glucose	1.1	1.5
fructose	1.1	0.6
sucrose	1.8	2.2
lactose	9.2	3.7

In Table 2 the experimental values of density (ρ), apparent molal volume of solute (ϕ_V), viscosity of the solution (η), and the relative viscosity of solution (η_r) of different carbohydrates in aqueous and 1.0 *m* aqueous urea solution at 318.15 K are listed. It is observed from Tables 1 and 2 that the value of ρ increases with the increase in concentration of the solute for all of the binary as well as ternary systems at both of the temperatures.

Figure 1 represents the variation in the apparent molal volume of solute (ϕ_V) against the molality of solute (m) for different carbohydrates in aqueous solutions at 308.15 K, whereas in Figure 2 the variation in the apparent molal volume of solute (ϕ_V) against the molality of solute (m) for different carbohydrates in 1.0 *m* aqueous urea solutions at 308.15 K is depicted. It is observed from these figures that the value of ϕ_V varies linearly with m for all of the systems at 308.15 K. The same type of behavior of $\phi_V - m$ is observed at 318.15 K also. The apparent molal volumes (ϕ_V^0) at infinite dilution were evaluated by smooth extrapolation of the apparent molal volume (ϕ_V) of solute to the zero concentration using the least-squares fitting method.

The values of ϕ_V^0 and S_V are collected in Table 3 for all of the carbohydrates in aqueous and 1.0 *m* aqueous urea solutions at different temperatures. It can be observed from Table 3 that the values of S_V are positive for all of the systems at both of the temperatures except for ternary mixture of lactose at 308.15 K, which is negative. It is also observed from Table 3 that the values of limiting apparent molal volume of solute (ϕ_V^0) in aqueous and 1.0 *m* aqueous urea solution for glucose are higher than that of fructose in aqueous and 1.0 *m* aqueous urea solution at both temperatures. The value of ϕ_V^0 for aqueous lactose solution is higher than sucrose solution at 308.15 K, but the reverse trend is observed at 318.15 K; that is, the value of ϕ_V^0 for aqueous lactose solution is lower than sucrose solution at this temperature. It is also observed that values of ϕ_V^0 for lactose in 1.0 *m* aqueous urea solution are higher than sucrose at both temperatures. Thus, it can be observed that the value of ϕ_E^0 are positive for all of the systems except for lactose in 1.0 *m* aqueous urea solution.

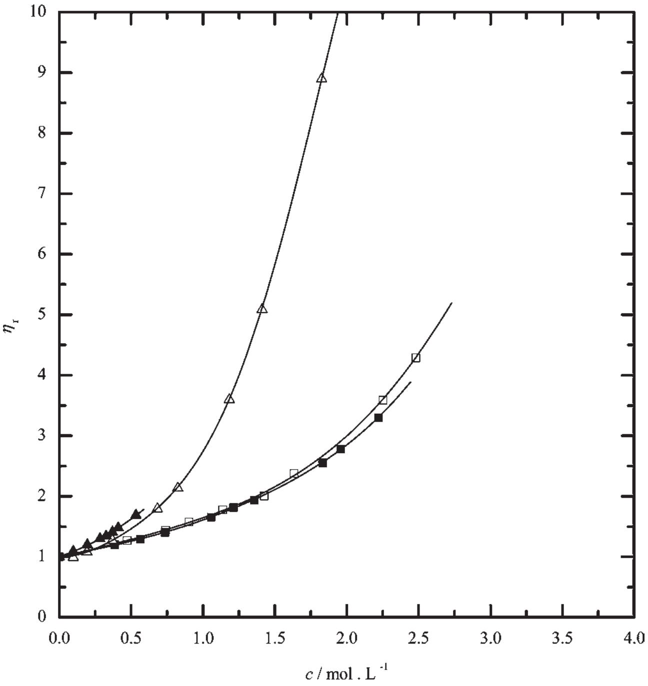

Figure 3. Plot of variation in the relative viscosity of solution (η_r) against the molarity of solute (c) in aqueous solution at 308.15 K. □—□, glucose + water; ■—■, fructose + water; △—△, sucrose + water; ▲—▲, lactose + water.

The values of partial molal volumes of transfer ($\Delta_{trans}\overline{V}_2^0$) at infinite dilution from water to 1.0 *m* aqueous urea solution are listed in Table 4. It is observed that $\Delta_{trans}\overline{V}_2^0$ values are positive for all of the solutes and the magnitude of value of $\Delta_{trans}\overline{V}_2^0$ increases for various carbohydrates in the order of fructose < glucose < sucrose < lactose. Franks et al.[26] have reported that the partial molal volume at infinite dilution of a nonelectrolyte is made up of an intrinsic molal volume (V_{int}) of the nonhydrated solute and a contribution due to the interaction of the solute with water, V_S:

$$\phi_V^0 = V_{\text{int}} + V_S$$

Edward and co-workers[27] and Arakawa et al.[28] have suggested that V_{int} is made up of two types of contributions.

$$V_{\text{int}} = V_{\text{V-W}} + V_{\text{void}}$$

where $V_{\text{V-W}}$ is the van der Waals volume and V_{void} is the associated void or empty volume.[29,30]

Edward et al.[27] have modified this equation to find the contribution of one molecule toward the partial molal volume of a hydrophilic solute as follows:

$$V_{\text{int}} = V_{\text{V-W}} + V_{\text{void}} - na_S$$

where a_S is the shrinkage in volume caused by interaction of hydrogen bonding groups with water molecules, and n is the potential number of hydrogen bonding sites in a molecule. Therefore, the partial molar volume of a sugar molecule can be represented as,

$$V_{\text{int}} = V_{\text{V-W}} + V_{\text{void}} - V_{\text{shrinkage}}$$

If one assumes that $V_{\text{V-W}}$ and V_{void} have the same magnitudes in water and aqueous urea solutions, the positive volume change accompanying the transfer of sugars from water to an aqueous urea solution may result from a decrease in the shrinkage in volume ($V_{\text{shrinkage}}$) because of interactions between urea and −OH groups of sugars. The interaction of urea with sugars diminishes further the structure-breaking effect of urea on water. In other words, more water is released as bulk water in the presence of sugars. Since bulk water has a higher volume contribution than broken structure water,[31] this factor may therefore contribute positively to the $\Delta_{\text{trans}}\overline{V}_2^0$ values.

Another way to express the solute−cosolute interactions is through the cosphere overlap model, where hydrophilic−hydrophilic type interactions contribute positively and hydrophobic−hydrophilic negatively to $\Delta_{\text{trans}}\overline{V}_2^0$ values.[32−35] The positive $\Delta_{\text{trans}}\overline{V}_2^0$ values obtained in this work (Table 4) for all of the sugars suggest that the former type of interactions dominate over the latter.[36]

The plots of variation of relative viscosity (η_r) against the molarity of solution (c) for different carbohydrates in aqueous solution at 308.15 K have been depicted in Figure 3. The variation of relative viscosity (η_r) against the molarity of solution (c) for different carbohydrates in 1.0 m aqueous urea solution at 308.15 K have been shown in Figure 4. It is seen from these figures that the value of η_r increases with an increase in the concentration of solute for both binary and ternary mixtures of carbohydrates. Similar trends are observed for these systems at 318.15 K also. The Jones−Dole equation viscosity B- and D-coefficients were obtained for these binary and ternary mixtures and are collected in Table 5. The temperature derivative of the B-coefficient, that is, dB/dT, for all of the systems are listed in Table 5. It has been reported that positive values of dB/dT represent the structure-breaking tendency, whereas negative

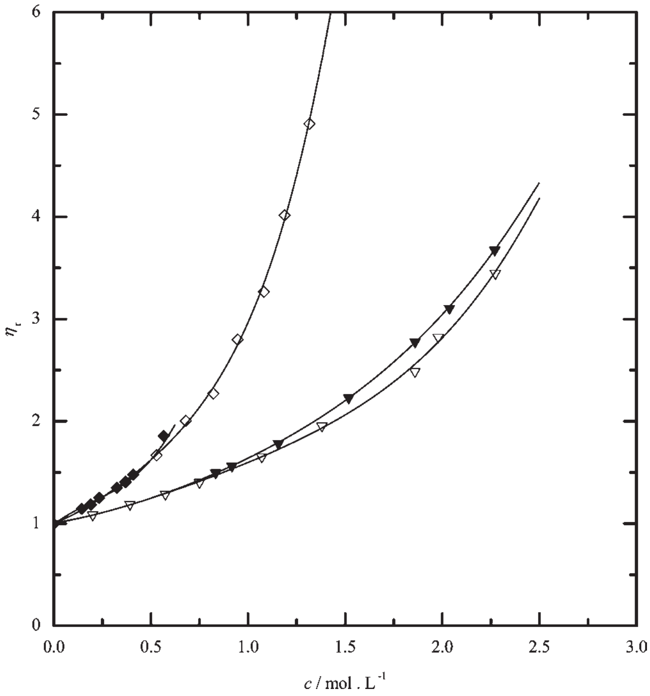

Figure 4. Plot of variation in the relative viscosity of solution (η_r) against the molarity of solute (c) in aqueous solution at 308.15 K. ▼—▼, glucose + 1.0 m aqueous urea solution; ▽—▽, fructose + 1.0 m aqueous urea solution; ◇—◇, sucrose + 1.0 m aqueous urea solution; ◆—◆, lactose + 1.0 m aqueous urea solution.

Table 5. Viscosity B- and D-Coefficients of Different Carbohydrates in Aqueous and 1 m Aqueous Urea Solution at Different Temperatures

	T = 308.15 K				T = 318.15 K				T = 313.15 K
	B	D			B	D			dB/dT
system	$L\cdot mol^{-1}$	$L^2\cdot mol^{-2}$	AAD	σ	$L\cdot mol^{-1}$	$L^2\cdot mol^{-2}$	AAD	σ	$L\cdot mol^{-1}\cdot K^{-1}$
glucose + water	0.141	0.498	−0.0099	0.0793	0.143	0.500	−0.0133	0.0831	0.0002
fructose + water	0.267	0.356	−0.0118	0.0428	0.278	0.285	−0.0011	0.0227	0.0011
sucrose + water	−0.969	2.995	0.0241	0.1599	−0.278	1.997	−0.0075	0.0981	0.0691
lactose + water	1.026	−0.529	0.0417	0.0800	0.138	1.368	0.0073	0.0241	−0.0888
glucose + 1 m aqueous urea solution	0.188	0.433	−0.0050	0.0280	0.255	0.356	0.0013	0.0094	0.0067
fructose + 1 m aqueous urea solution	0.214	0.393	−0.0133	0.0625	0.231	0.340	−0.0087	0.0353	0.0017
sucrose + 1 m aqueous urea solution	−0.112	2.430	−0.0231	0.1172	−0.189	2.101	−0.0071	0.0746	−0.0077
lactose + 1 m aqueous urea solution	1.067	−0.697	0.0513	0.0930	0.225	1.483	0.0076	0.0134	−0.0842

dB/dT values indicate the structure-making tendency of the solute in the mixture.[37] It is observed from the above table that for glucose + water and fructose + water systems, the values of dB/dT are positive, and further, the value of dB/dT increases in 1.0 m aqueous urea solution for these carbohydrates. The above observation suggests that glucose molecules occupies the cavity of the water molecules without disturbing solvent structure to a large extent in the binary mixture but behave as a weak structure breaker in the 1.0 m aqueous urea solution. Further, seen in this context the small change in the values of dB/dT for fructose in aqueous binary as well as in 1.0 m aqueous urea solutions suggests that the interactions of this monosaccharide molecules with water molecules are not affected to a large extent when urea is added as a cosolute to the aqueous solution. For the sucrose + water binary system, the value of dB/dT was found to be positive and is higher than glucose and fructose in binary and ternary systems. This is expected as sucrose is made of glucose and fructose units. However, the value of dB/dT was observed to be negative for sucrose in 1.0 m aqueous urea solution. Seen in this context, sucrose behaves as a stronger structure breaker as compared to monosaccharide in binary aqueous medium but acts a weaker structure maker in 1.0 m aqueous urea solution. This indicates that the water structure around solute gets enhanced when urea is added to water. The values of dB/dT for lactose + water and lactose + 1.0 m aqueous urea solutions are negative. This suggests that lactose acts as a structure maker in aqueous as well in 1m aqueous urea solutions. This is a significant observation. Kaulgud and Dhondge[10] also observed that lactose, when dissolved in water, is more hydrated as compared to sucrose.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental data summary. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: s_dhondge@hotmail.com.

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