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Intermolecular Forces of Sugars in Water

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Summary. Apparent molar volume and viscosities of fructose, glucose, mannose, and sucrose have been measured in dilute aqueous solution, concentration range 0.028–0.336 M at 293 K. The viscosity coefficient B and A were calculated from the viscosity data using the *Jones-Dole* equation for all the studied sugars. The data were also analysed for *Stauarding* equation. The structure making behavior was obtained for all the sugars. A modified *Jone-Dole* equation was proposed by using ratio of mole fractions of solute and solvent in place of concentrations of solute.

Keywords. Viscosity co-efficient; Apparent molar volume; Modified *Jone-Dole* equation; Supramolecular chemistry; Density.

Introduction

The molecular interactions of sugars in dilute aqueous solution plays an important role in governing the biological and medicinal mechanism of any system. The determination of apparent molar volume and viscosity are used as guide to study the structural properties and solute-solvent interactions of solutions. *Kaulgud* and *Dhondge* [1] reported the apparent molar volume of some carbohydrates in dilute aqueous solutions and results are discussed along with measured sound velocities. *Blokhra* and *Kumar* [2] measured the viscosities of 1:1 electrolytes in aqueous dextrose at concentration range 0.01–1.00 M and results were discussed from the viewpoint of *Jone-Dole* equation. Studies on viscosity and density of sucrose and maltose have been made in aqueous ammonium chloride solution at different temperatures [3]. The behavior of carbohydrates has been measured in water with co-solvent and results were analysed for solvent interactions in terms of molar volume [4]. The aqueous solutions of sugars have been used by many workers in studying solute-solvent interactions in aqueous and mixed solvent systems [5–10]. In the present study monosaccharides and a disaccharide have been investigated because coverage of the disaccharide which can be formed by condensation can be useful to discuss the overall aspects of interactions measured by volumetric and viscosimetric methods.

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Results and Discussion

The observed densities of the sugar solutions are used to calculate apparent molar volume (Φ_v) of sugar using Eq. (1), where d_0 is the density of solvent, d is the density of the sugar solution, M is molecular weight, and C is the concentration (mol dm^{-3}).

$$\Phi_v = \frac{M}{d_0} - \frac{1000(d - d_0)}{Cd_0} \qquad (1)$$

The calculated values of Φ_v at different concentrations of sugars are given (Table 1). The limiting apparent volume Φ_v^o were obtained by the methods of least squares. For the extrapolatation of Φ_v *versus* $\sqrt{C}$ to zero concentration, the points of low concentration that deviated considerable from linearity were not considered. The value of the intercept was computed by using the *Messon*'s relation given by Eq. (2).

$$\Phi_v = \Phi_v^o + S_v\sqrt{C} \qquad (2)$$

The values of Φ_v^o and S_v for the sugars at 293 K are given in Table 1. The value of Φ_v^o and S_v were calculated with the help of computer using the relation of Eq. (2). The Φ_v^o values are positive for all the sugars indicating thereby positive interaction between solute and solvent molecules. The value S_v is positive only for **4**, which indicates that there is a quite strong interaction between two monomeric units of sugars present in the molecule of **4**. The values of Φ_v^o obtained in this study are almost the same as reported in the work of *Kaulgud* and *Dhondge* with a variation of ±1.5% Table 1.

The relative viscosity of the sugars' solutions at different concentrations in H_2O was calculated assuming that the sugar molecules behave like a monomer unit of a polymolecular assembly. Thus if η is the viscosity of the solutions of solute

Table 1. Apparent molar volumes Φ_v for sugars at 293 K at different concentration

Concentration (mol dm^{-3})	$\sqrt{C}$	Φ_v (cm^3 mol^{-1})			
		Glucose	Fructose	Mannose	Sucrose
0.028	0.1673	112.34	108.46	116.31	203.08
0.056	0.2366	112.34	110.55	117.71	206.66
0.084	0.2898	112.34	109.72	117.11	211.43
0.112	0.3347	112.34	109.66	118.16	205.77
0.140	0.3742	111.62	109.48	116.63	208.09
0.168	0.4049	111.74	109.36	117.11	213.22
0.196	0.4427	111.83	109.79	116.43	211.77
0.224	0.4733	114.13	109.66	116.37	209.79
0.252	0.5020	111.54	109.70	116.71	208.25
0.280	0.5292	110.91	109.12	116.65	214.18
0.308	0.5550	111.37	109.09	116.91	209.70
0.336	0.5797	111.15	109.06	116.52	219.18
Φ_v^o (cm^3 mol^{-1})		113.10	109.68	117.13	202.74
S_v (cm$^{3/2}$ mol$^{3/2}$)		−3.23	−8.78	−0.77	16.58

Table 2. Relative viscosities (η/η_0) for sugar at 293 K at different concentration

Concentration (mol dm^{-3})	$\sqrt{n_s/n_w}$ for monosaccharides	(η/η_0) for monosaccharides			(η/η_0) for disaccharide (Sucrose)	
		Glucose	Fructose	Mannose	$\sqrt{n_s/n_w}$	(η/η_0)
0.028	0.0224	1.008	1.013	1.015	0.0224	1.026
0.056	0.0316	1.019	1.026	1.030	0.0316	1.050
0.084	0.0387	1.034	1.039	1.045	0.0387	1.079
0.112	0.0447	1.050	1.052	1.060	0.0458	1.112
0.140	0.0510	1.065	1.065	1.075	0.0510	1.128
0.168	0.0548	1.081	1.078	1.090	0.0610	1.160
0.196	0.0600	1.096	1.091	1.110	0.0648	1.195
0.224	0.0632	1.111	1.104	1.116	0.0651	1.230
0.252	0.0678	1.127	1.118	1.32	0.0692	1.275
0.280	0.0735	1.43	1.32	1.148	0.0734	1.308
0.308	0.0755	1.160	1.147	1.164	0.0768	1.343
0.336	0.0794	1.175	1.163	1.185	0.0806	1.378

(polymer) and η_0 is the viscosity of the pure solvent at constant temperature, the polymeric species follow the Eq. (3) given by *Staurding* [11].

$$\frac{\eta - \eta_0}{\eta_0} = kn\,Cn \tag{3}$$

In Eq. (3) k is a constant for a given solute in a given solvent, C is the molar concentration of monomer, and n is the number of monomers in the polymer. The observed relative viscosity values are given in Table 2.

The observed data were used to examine how far the results of viscosities of sugar solutions agree with Eq. (3) applicable for polymers/colloidal molecules. Therefore the relative viscosity values were plotted against different concentrations of sugars and for all the sugars these plots show linearity having a minimum intercept value at zero concentration. The values of gradient (kn) obtained for different sugars are given in Table 3. The structure making and structure breaking properties of sugars in solutions as reported in organic solvents [4] have been taken

Table 3. Values of parameters of *Staurding*, *Jone-Dole*, and modified *Jone-Dole* equation for the sugars at 293 K in aqueous solution

Sugars	$(\eta/\eta_0 - 1)$ *versus* C	$(\eta/\eta_0 - 1)\sqrt{C}$ *versus* $\sqrt{C}$	$(\eta/\eta_0 - 1)/\sqrt{n_s/n_w}$ *versus* $\sqrt{n_s/n_w}$
Glucose	$kn = 0.55\,\text{dm}^3\,\text{mol}^{-1}$	$B = 0.63\,\text{dm}^{3/2}\,\text{mol}^{-1}$ $A = -0.062\,\text{dm}^{3/2}\,\text{mol}^{-1/2}$	$B_x = 32.93$ $A_x = -0.384$
Fructose	$kn = 0.40\,\text{dm}^3\,\text{mol}^{-1}$	$B = 0.48\,\text{dm}^{3/2}\,\text{mol}^{-1}$ $A = -0.016\,\text{dm}^{3/2}\,\text{mol}^{-1/2}$	$B_x = 25.38$ $A_x = 0.015$
Mannose	$kn = 0.54\,\text{dm}^3\,\text{mol}^{-1}$	$B = 0.53\,\text{dm}^{3/2}\,\text{mol}^{-1}$ $A = 0.000\,\text{dm}^{3/2}\,\text{mol}^{-1/2}$	$B_x = 27.69$ $A_x = 0.081$
Sucrose	$kn = 1.15\,\text{dm}^3\,\text{mol}^{-1}$	$B = 1.22\,\text{dm}^{3/2}\,\text{mol}^{-1}$ $A = 0.80\,\text{dm}^{3/2}\,\text{mol}^{-1/2}$	$B_x = 61.46$ $A_x = -0.359$

into account in terms of viscosity coefficient B and data were analysed according to *Jone-Dole* (Eq. (4)).

$$\frac{\eta}{\eta_0} = 1 + A + B\sqrt{C} \tag{4}$$

In Eq. (4) η/η_0 is the relative viscosity, C is the molar concentration of solute, and A and B are constants. A plot of $(\eta/\eta_0 - 1)/\sqrt{C}$ *versus* $\sqrt{C}$ is linear with slope B and intercept A. The values of A and B are given in Table 3 for each sugar studied. Equation (4) is more useful in case of ionic solute because A represents the contribution from interionic electrostatic force. In the present study for sugars the possibility of interionic interaction is very small in comparison to the intermolecular attractions between solute and solvent. Hence the analysis of the viscosity data in terms of Eq. (4) in which we have used ratio of mole fractions of solute and solvent n_s/n_w in place of concentration, the plot $(\eta/\eta_0 - 1)/\sqrt{n_s/n_w}$ *versus* $\sqrt{n_s/n_w}$ also showed linear relation. The values of intercept and slope of such plots are also given in Table 3.

It is evidented from the results (Table 3), that the values of coefficients B are positive for all the sugars studied in aqueous dilute solutions indicating that solute-solute interaction/solute-solvent interactions are more significant and all the sugars behave as "structure makers". The value of A is negative for **1**, **2**, and **3** but it is positive for **4** due to interaction between two monomeric units present and a greater number of hydroxyl groups in the disaccharide unit. The Φ_v^o values for all the sugars are positive which suggest that all the sugars interact with water molecules through dipole-dipole interactions of the hydroxyl groups present in the sugar molecule. Viscometric and volumetric properties indicate the same behavior of sugar molecules in dilute aqueous solution.

The observed constants k when $n = 1$ for **1**, **2**, and **3** have nearly almost the same value (0.40–0.55) because all three have same number of OH groups and they all are monosaccharides. In case of **4** which is a disaccharide the kn value is (1.15), which can be justified with the values of monosaccharides only when we consider $n = 2$. The relationship considered in Eq. (3) is also applicable for the class of sugars on the basis of which we can conclude that the sugar molecules also behave like polymolecular assemblies/polymers in aqueous solution. In the analysis of results with computer a negative value of intercept (10^{-2}) was insignificant. In our study we have proposed a modification in the *Jone-Dole* equation by using n_s/n_w in place of concentration of solute because the term n_w includes the reorientation of solvent molecules which are also responsible for solute-solute and solute-solvent interaction. The relationship proposed is in good agreement with the original equation in linearity but the slope values B_x are very large in magnitude (50–63 times). With the objectives in mind the slope value in the original equation is a measurement of solute property in solution, the proposed modified equation gives more accurate results due to enhancement in measurable value of slopes as obtained in the present study. The proposed modified *Jone-Dole* equation is given by Eq. (5).

$$\frac{\frac{\eta - \eta_0}{\eta_0}}{\sqrt{n_s/n_w}} = A_x + B_x\sqrt{n_s/n_w} \tag{5}$$

In Eq. (5) n_s is the mol fraction of solute and n_w is the mol fraction of solvent (H_2O).

Experimental

Sugars, *viz.* 1,3,4,5,6-pentahydroxyl-2-hexanone (**1**, $C_6H_{12}O_6$, *D*-fructose), 2,3,4,5,6-pentahydroxyhexanal (**2**, $C_6H_{12}O_6$, *D*-glucose), 2,3,4,5,6-pentahydroxyhexanal (**3**, $C_6H_{12}O_6$, *D*-mannose epimer of *D*-glucose), and 2-(1,3,4,6-tetrahydroxyl-1,5-oxy-hexanoxy)-2,5-oxyhexane-1,3,4,6-tetraol (**4**, $C_{12}H_{22}O_{11}$, sucrose), of AR grade were used as such without further purifications. Freshly prepared distilled conductivity water (specific conductivity $10^{-6}\,\mathrm{S\,cm^{-1}}$) was used for preparing aqueous solutions. The sugar solutions of different concentrations in the range 0.028–0.336 *M*) were prepared by dissolving required weight of sugar in a known volume of H_2O on molarity basis. The pyknometer was used to determine the densities of the solutions. Density reading was precise up to $0.0001\,\mathrm{g\,cm^{-3}}$ checked by weighing for known volume with the help of an electronic signal pan balance (Afcoset make). The viscosity of the solutions was measured by using Ubbelhode viscometer. The uncertainties in the measured viscosities were ±0.05%. All the measurements have been carried out at 293 K on a water bath thermostatically controlled within ±0.01°C.

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