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

Koichiro MIYAJIMA,* Masahiro SAWADA, and Masayuki NAKAGAKI
Faculty of Pharmaceutical Sciences, Kyoto University, Yoshida Shimoadachi-cho, Sakyo-ku, Kyoto 606

(Received January 14, 1983)

Viscosities, apparent molar volumes, and activity coefficients of aqueous solutions for D-glucose, maltose, and maltotriose were measured at various concentrations. The signs of B_{st}, the increment of viscosity *B*-coefficient arising from structural change of water, were positive for these three saccharides, and the signs of dB/dT, the temperature dependence of *B*, were negative. The magnetudes of B_{st} and $|dB/dT|$ increased with the number of glucose residue. Activity coefficients were larger than unity and increased with concentration, and their magnitudes also increased with the number of glucose residue. These results indicate that D-glucose, maltose, and maltotriose are structure forming solutes, and that their abilities lie in the order of D-glucose<maltose<maltotriose.

Many studies[1,2] concerning the properties of aqueous solutions of saccharides have been published, because they are not only biochemically important compounds but also the typical nonelectrolytes with hydrophilic hydoxyl groups, which are capable of hydrogen bonding. Stokes and Robinson[3] interpreted the concentration dependences of activity coefficients of D-glucose and sucrose in terms of the semi-ideal solution theory.[†] This idea that the solute-solvent interactions govern the concentration dependences of thermodynamic quantities seems to be fundamentally correct, since Raman[4] and NMR relaxation[5] studies of aqueous solutions of mono- and disaccharides suggested an absence of solute-solute interactions even at relatively high concentrations.

Kabayama and Patterson[6] postulated that not only the number of hydroxyl groups but also the stereochemical orientation of hydroxyl groups, *i.e.* axial and equatorial, play an important role on the hydration of saccharides. In other words, the spacing of oxygen atoms of equatorial OH groups of monosaccharides in chair conformation nearly fit the spacing of oxygen atoms of ice-like structure of water. This hydration model for saccharides is so called "specific hydration model." The people who favour this model, Franks school of England, regard monosaccharide, which takes mainly the chair conformation, as a structure maker. Harvey *et al.*[7] are suspicious of the validity of this model because of the similarity of NMR spectra of monosaccharides between aqueous and alcoholic solutions. Rowlinson *et al.*[8] and Kawaizumi *et al.*[9] classified mono- and disaccharides as structure makers in terms of excess partial molar entropy and heat capacity. While Goring *et al.*[10] classified the hydrophilic solutes including D-glucose and sucrose as structure breakers, on the basis of positive temperature dependences of apparent molar volumes.

To solve the puzzling situation of the effect of saccharide on water structure, we measured viscosity *B*-coefficients, apparent molar volumes and activity coefficients of D-glucose homologues; D-glucose, maltose and maltotriose, and discussed the effects of these compounds on water structure.

Experimental

Materials. Reagent grade D-glucose, maltose, and maltotriose purchased from Nakarai Chemical Co. Ltd., were dried *in vacuo* over P_2O_5 at room temperature for several days before use. Under these conditions, the water of hydration of maltose monohydrate was reported to be stable.[11] Reagent grade sodium chloride obtained from Matsunaga Chemical Co. Ltd., was dried *in vacuo* at 110 °C for a day. These compounds are dissolved in purified water by distillations and deionization.

Method. The viscosity measurements were carried out at 15, 25, and 35±0.03 °C using an Ostwald type viscometer with an efflux time of *ca.* 540 s for water at 25 °C. The detail procedure and kinetic correction of viscometer were described elsewhere.[12] The experimental determination of an efflux time was precise to ±0.05 s.

Density of a solution was measured by Seiko SDM 420 and 421 vibration densimeter at 15, 25, and 35±0.01 °C. Pure water and 6 mol dm^{-3} aqueous sodium chloride solution were used as the standards for the calibration of the apparatus. Measurements were done at least twice for every solution and were accurate within $\pm 10^{-5}$ g cm^{-3}. Apparent molar volume, ϕ_V of solute was calculated by Eq. 1.

$$\phi_V = 1000(d_0 - d)/cd_0 + M_2/d, \tag{1}$$

where d_0 and d are the densities of solvent and solution, respectively. M_2 is molecular weight of solute.

Osmotic coefficients of maltose and maltotriose were measured at 25±0.02 °C by isopiestic comparison method described elsewhere.[13] Sodium chloride was used as a reference solute. Experimental determination of isopiestic concentration was precise to ±0.2%.

Results and Discussion

Relative viscosity, η_{rel}, of nonelectrolyte solution in relatively high concentration range (0.1—1.0 mol dm^{-3}) is expressed by

$$\eta_{rel} = \eta/\eta_0 = 1 + Bc + Dc^2, \tag{2}$$

where η_0 and η are the viscosities of solvent and solution, respectively, and c is the molarity of solute. At constant pressure and temperature, *B* and *D* are the characteristic constants depending on the combination of solute and solvent. The constant *B* is so called "viscosity *B*-coefficient", which is related to the solute-solvent interaction. The constant *D* is the coefficient

---

[†] Water molecules and hydrated saccharide molecules mix ideally.

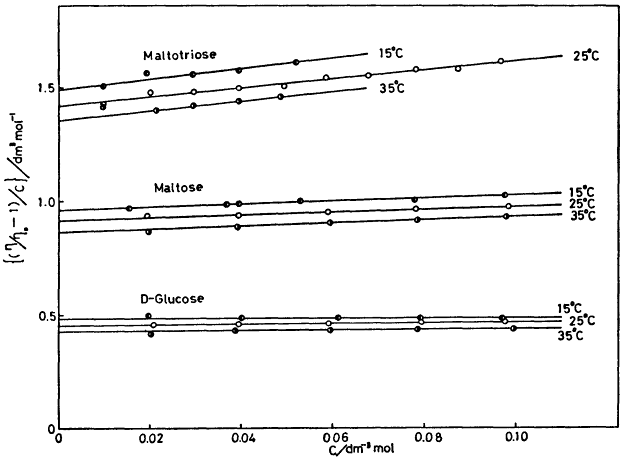

Fig. 1. Relations between $(\eta/\eta_0-1)/c$ and c for saccharides at 15, 25, and 35 °C.

representing the interactions of solute-solvent and solute-solute, but the physical meaning of D-coefficient is not yet clarified.

As shown in Fig. 1, B and D coefficients are obtained from the intercepts and the slopes of $(\eta_{\mathrm{rel}}-1)/c$ *vs.* c curves. B-coefficient is usually expressed by the sum of two terms, *i.e.* B_{size} and B_{st}. The former is the contribution of hydrodynamic obstruction effect arising from the size and the shape of solute molecule, and the latter the contribution of the structural change of solvent by solute-solvent interactions. For the estimation of B_{size}, the Einstein-Simha viscosity equation for colloidal suspension is usually applied to the solution of low molecular weight solute.

$$\eta_{\mathrm{rel}} = 1 + \nu\phi, \qquad (3)$$

where ϕ is the volume fraction of colloidal particle and ν is a function of the axial ratio of ellipsoid. The ν value is equal to 2.5 for spherical colloidal suspension, which corresponds to the Einstein equation. Assuming that the effective rigid volume of solute equals to the partial molar volume of solute at infinite dilution ($\overline{V}^{\circ}$), ϕ is equal to $c\overline{V}^{\circ}/1000$. Hence B_{st} can be expressed by

$$B_{\mathrm{st}} = B - \nu\overline{V}^{\circ}/1000. \qquad (4)$$

Scheraga's table[14] was combined with the axial ratio of oblate given by Edward[15] to obtain the ν value for D-glucose. We adopted the ν values of cellobiose and cellotriose as those of maltose and maltotriose. The values of $\overline{V}^{\circ}$ were obtained from the densities of the solutions described later.

The temperature dependences of B-coefficients for three saccharides are shown in Fig. 2. Each slope of the curves ($\mathrm{d}B/\mathrm{d}T$) is negative, and the absolute values increase with the number of glucose residue. The values of B at 15, 25, and 35 °C, and the values of B_{st} and $\mathrm{d}B/\mathrm{d}T$ at 25 °C are listed in Table 1. The values of B and $\mathrm{d}B/\mathrm{d}T$ for D-glucose are in fair agreement with those calculated from Goring's data[16]. As seen in Table 1, the positive signs of B and the negative signs of $\mathrm{d}B/\mathrm{d}T$ indicate that these solutes are structure makers. As shown in Fig. 3(a), the negative values of $\mathrm{d}B/\mathrm{d}T$ increase with the number of glucose residue (n). It is noteworthy that the intercept of the straight line drawn through the three points gives positive value in $\mathrm{d}B/\mathrm{d}T$ *vs.* n plots. This fact means the structure making effects of maltose and maltotriose are not twice and three times as large as that of D-glucose, indicating that the formation of α-1,4 linkage reduces the structure making effects of saccharides.

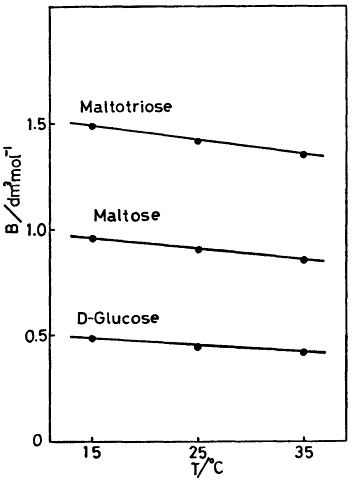

Fig. 2. Temperature dependences of B-coefficients for saccharides.

Table 1. The values of B, B_{st}, $\mathrm{d}B/\mathrm{d}T$, $\overline{V}^{\circ}$, and α^* for saccharides

	Temp/°C	D-Glucose	Maltose	Maltotriose
$B/\mathrm{dm^3\,mol^{-1}}$	15	0.49	0.96	1.49
	25	0.45	0.91	1.42
	35	0.43	0.86	1.36
$B_{\mathrm{st}}/\mathrm{dm^3\,mol^{-1}}$	25	0.14	0.31	0.41
$\frac{(\mathrm{d}B/\mathrm{d}T)\times 10^3}{\mathrm{dm^3\,mol^{-1}\,K^{-1}}}$	25	−3.0	−5.0	−6.5
$\overline{V}^{\circ}/\mathrm{cm^3\,mol^{-1}}$	15	110.3	205.5	304.0
	25	111.3	209.0	309.0
	35	112.5	211.0	312.5
$\frac{\alpha^*\times 10^3}{\mathrm{cm^3\,mol^{-1}\,K^{-1}}}$	25	1.0	1.3	1.4

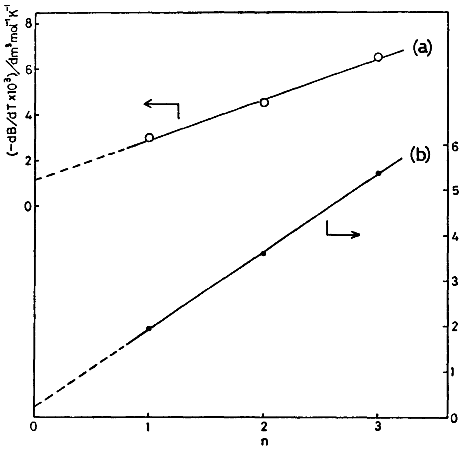

Fig. 3. Plots of $\mathrm{d}B/\mathrm{d}T$ (a) and h (b) against n.

Apparent molar volume of nonelectrolyte is expressed by

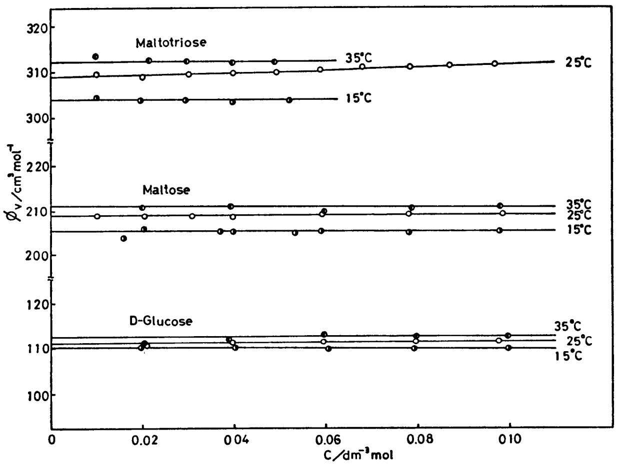

Fig. 4. Relations between ϕ_V and c for saccharides at 15, 25, and 35 °C.

$$\phi_V = \overline{V}^\circ + b_V c, \tag{5}$$

where $\overline{V}^\circ$ is the partial molar volume at infinite dilution and b_V is an empirical constant reflecting the solute-solute interactions. As shown in Fig. 4, ϕ_V values for three saccharides at 15, 25, and 35 °C are linearly related to the concentration. The slopes of ϕ_V *vs. c* curves correspond to b_V, which are nearly zero at 15 °C and slightly positive at 25 and 35 °C. The small values of b_V indicate that the solute-solute interactions are weak in the systems. Table 1 shows the partial molar volumes at infinite dilution at 15, 25, and 35 °C and the coefficients of thermal expansion (α^*) at 25 °C. The values of $\overline{V}^\circ$ for these three saccharides at 25 °C are in fair agreement with the literature.[11] The volume increment for glucose residue is about 100 cm³ mol⁻¹. α^* values were calculated by Eq. 6.

$$\alpha^* = (\mathrm{d}\overline{V}^\circ/\mathrm{d}T)/\overline{V}^\circ. \tag{6}$$

The values of α^* increase with the number of glucose residue, indicating that the amount of unstructured water per glucose residue increases with the number of glucose residue, because the expansibility of disordered water must be larger than that of structured water.

TABLE 2. OSMOTIC AND ACTIVITY COEFFICIENTS FOR SACCHARIDES AT 25 °C

	Maltose		Maltotriose	
m	ϕ	γ	ϕ	γ
0.1	1.002	1.003	1.002	1.003
0.2	1.004	1.007	1.006	1.010
0.3	1.006	1.010	1.010	1.016
0.4	1.010	1.014	1.016	1.023
0.5	1.015	1.020	1.022	1.030
0.6	1.021	1.027	1.030	1.040
0.7	1.028	1.036	1.038	1.049
0.8	1.035	1.044	1.048	1.061
0.9	1.042	1.052	1.059	1.074
1.0	1.050	1.061	1.071	1.088
1.1	1.058	1.070	1.084	1.103
1.2	1.067	1.081	1.098	1.120
1.3	1.076	1.091	1.113	1.138
1.4	1.086	1.103	1.129	1.158
1.5	1.096	1.114	1.146	1.179
1.6	1.106	1.126	1.162	1.199
1.7	1.116	1.138	1.179	1.220
1.8	1.126	1.150	1.196	1.242
1.9	1.137	1.163	1.213	1.265
2.0	1.148	1.176	1.231	1.288

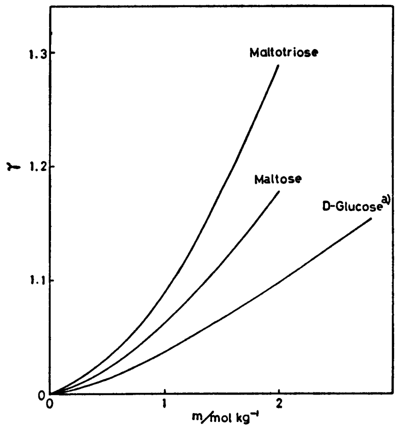

Fig. 5. Activity coefficients of saccharides at 25 °C.
a) see Ref. 2.

Osmotic (ϕ) and activity (γ) coefficients for maltose and maltotriose are shown in Table 2. The values of ϕ for maltose are in fair agreement with those reported by Uedaira.[17] As seen in Fig. 5, activity coefficients for three saccharides increase with concentration and their magnitudes lie in the order of D-glucose<maltose<maltotriose. The fact that activity coefficients for these saccharides are larger than unity implies that strong solute-solvent interactions exist in these solutions, since solute-solute interactions are weak or absent.[4,5] Using the following equation derived from the semi-ideal theory,

$$\phi = -\frac{1}{0.018m}\ln\left[\frac{1-0.018mh}{1-0.018m(h-1)}\right], \tag{7}$$

the hydration numbers (h) for these saccharides were calculated from osmotic coefficients at 2 mol kg⁻¹, and relation between h and n is shown in Fig. 3(b). The hydration number increases linearly with the number of glucose residue (n), indicating that the hydration number per glucose residue is nearly constant among these low molecular weight homologues. The point given by extrapolating the straight line to $n=0$ shows the positive value. As seen in Fig. 3(a), this behavior is similar to the relation between $\mathrm{d}B/\mathrm{d}T$ and n, and indicates that the formation of α-1,4 ether linkage from the two monosaccharides results in the decrease of hydration numbers of saccharides. The possible explanation for these results may be due to the decrease of the sites of hydrogen bond and/or the increase of structural incompatibility by the formation of α-1,4 ether linkage, because the disagreement of geometric factors of oligosaccharide with ice-like structure of water is considered to occur due to the fact that C–O–C linkage has two degrees of rotational freedom.

Judging from the specific hydration model, it seems to be reasonable that the value of dB/dT or hydration number per glucose residue decrease with increase of the number of glucose residue, because the incompatibility of orientation of hydrogen bond between a saccharide molecule and water molecules of ice-like structure would increase with the number of α-1,4 ether linkage as stated above.

As seen in Fig. 3, however, the value of dB/dT or hydration number is nearly proportional to the number of glucose residue. This result implies that the hydration behavior of di- and trisaccharides are more consistent with the prediction of simple hydration model[††] rather than that of the specific hydration model. As stated previously, the validity of the specific hydration model for monosaccharide solutions is still in controversy. Our results seem to indicate the inadequacy of the specific hydration model for the application of oligosaccharide solutions.

Based on the results of viscosity B-coefficients, apparent molar volumes, and activity coefficients, these saccharides are structure forming solutes, and their abilities lie in the order of D-glucose<maltose<maltotriose.

[††] The hydration number of saccharide depends on the number of hydroxyl group in the molecule at the constant water activity.1)

References

1) A. Suggett, "Water, A Comprehensive Treatise," ed by F. Franks, Plenum Press, New York (1975), Vol. 4, p. 533.

2) K. Miyajima, M. Sawada, and M. Nakagaki, this Bulletin submitted.

3) R. H. Stokes and R. A. Robinson, *J. Phys. Chem.*, **70**, 2126 (1966).

4) G. A. Walrafen, *J. Chem. Phys.*, **44**, 3726 (1966).

5) A. Sugget, S. Albett, and P. J. Lillford, *J. Solution Chem.*, **5**, 17 (1976).

6) M. A. Kabayama and D. Patterson, *Can. J. Chem.*, **36**, 563 (1958).

7) J. M. Harvey and M. C. R. Symons, *J. Solution Chem.*, **7**, 571 (1978).

8) J. B. Taylor and J. S. Rowlinson, *Trans. Faraday Soc.*, **51**, 1183 (1955).

9) F. Kawaizumi, N. Nishio, H. Nomura, and Y. Miyahara, *J. Chem. Thermodyn.*, **13**, 89 (1981).

10) J. L. Neal and D. A. I. Goring, *J. Phys. Chem.*, **74**, 658 (1970).

11) F. Shahidi, P. G. Farrell, and J. T. Edward, *J. Solution Chem.*, **5**, 807 (1976).

12) K. Miyajima, M. Sawada, and N. Nakagaki, *Bull. Chem. Soc. Jpn.*, **55**, 3101 (1982).

13) K. Miyajima, K. Inari, N. Hamaguchi, H. Yoshida, and M. Nakagaki, *Nippon Kagaku Kaishi*, **1975**, 1447.

14) H. A. Scheraga, *J. Chem. Phys.*, **23**, 1526 (1955).

15) J. T. Edward, *Can. J. Chem.*, **35**, 571 (1957).

16) M. Ihnat, A. Szabo, and D. A. I. Goring, *J. Chem. Soc., A*, **1968**, 1500.

17) H. Uedaira and H. Uedaira, *Bull. Chem. Soc. Jpn.*, **42**, 2137 (1969).