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Studies on Aqueous Solutions of Saccharides. I. Activity Coefficients of Monosaccharides in Aqueous Solutions at 25 °C

Koichiro Miyajima,* Masahiro Sawada, and Masayuki Nakagaki
Faculty of Pharmaceutical Sciences, Kyoto University, Yoshida Shimoadachi-cho, Sakyo-ku, Kyoto 606

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Activity coefficients of isomeric monosaccharides, D-glucose, D-mannose, and D-galactose were determined by isopiestic comparison method at 25 °C. Excess partial molar entropy of water ($\bar{S}_w^{ex}$) of each monosaccharide solution was negative and the absolute value increased with concentration of solute. From the magnitudes of negative $\bar{S}_w^{ex}$, it was concluded that the structure making ability among three isomers lies in the order D-glucose> D-mannose>D-galactose.

Many papers have been published on the properties of aqueous solutions of monosaccharides, because they are not only biologically important compounds but also the typical hydrophilic nonelectrolytes in the field of solution chemistry.

On the hydration of monosaccharides, Kabayama and Patterson[1] postulated that the spacing of oxygen atoms of equatorial hydroxyl groups of hexopyranose in chair conformations, which are predominant in aqueous solution, are compatible to the spacing of oxygen atoms in tridymite-like structure of water. This model is a so called "specific hydration model."[4] To investigate the validity of the hypothesis, various kinds of experiments, such as partial molar volume,[2,3] compressibility,[2,3] ^{1}H- and ^{17}O-NMR[4-7] and dielectric relaxation[4,8] were carried out. However their conclusions are still in controversy.

From the similar viewpoint, we determined the activity coefficients of three isomeric monosaccharides, *i.e.* D-glucose, D-mannose, and D-galactose in aqueous solution at 25°C and calculated the excess partial molar entropy of water ($\bar{S}_w^{ex}$) from the excess free energy combining the excess enthalpy data[9,10] and investigated the correlation between $\bar{S}_w^{ex}$ and the structure making ability predicted by the special hydration model.

Experimental

Materials. Reagent grade D-glucose, D-mannose, and D-galactose obtained from Wako Chemical Co. Ltd., were dried over P_2O_5 *in vacuo* at room temperature for several days. Reagent grade $CaCl_2 \cdot 2H_2O$ was used without further purification. These compounds were dissolved in purified water by distillation and deionization.

Method. Osmotic coefficients were determined at 25±0.02 °C by isopiestic comparison method described elsewhere.[11] From the osmotic coefficient (ϕ), activity coefficient (γ) was calculated by

$$\ln \gamma = (\phi - 1) + \int_0^m \frac{\phi - 1}{m} \mathrm{d}m, \tag{1}$$

where m is the molality of solute. Buoyancy correction was made for monosaccharides assuming that the densities of the solutes in solid states were unity. Experimental determination of isopiestic concentration was precise to ±0.2%. The molalities of isopiestic solution are shown in Table 1. The concentration of $CaCl_2$ used as a reference solute was determined by gravimetric analysis with silver nitrate.

Results and Discussion

Osmotic and activity coefficients of D-monnose and D-galactose are shown in Table 2 together with those of D-glucose. The values of ϕ and γ of D-glucose obtained from this experiment are in a fair agreement with those of Taylor and Rowlinson,[12] but are larger than those of Bonner and Breazeale.[13] The values of γ for three monosaccharides lie in the order D-glucose>D-galactose>D-mannose.

The standard states are taken asymmetrically; taking the infinite dilution and the pure solvent as the standard states of the solute and solvent, respectively, the total excess Gibbs free energy of solution containing a kilogram of solvent is calculated from ϕ and γ by Eq. 2.[14]

$$G^{ex} = mRT(1 - \phi + \ln \gamma). \tag{2}$$

From the heat of dilution of monosaccharides, excess enthalpy of solution (H^{ex}) is expressed in the following form,[9]

$$H^{ex} = h_{xx}m^2 + h_{xxx}m^3, \tag{3}$$

where h_{xx} and h_{xxx} are the interaction parameters. Excess entropy of solution (S^{ex}) is calculated by Eq. 4.

$$S^{ex} = (H^{ex} - G^{ex})/T. \tag{4}$$

Excess quantities *vs.* concentration curves for three monosaccharides are shown in Figs. 1, 2, and 3. The small value of positive excess free energy comes from the difference between largely positive enthalpy and entropy term, that is, the entropy-enthalpy compensation takes place in each system. The predominance of enthalpy term over entropy term characterizes hydrophilic solute in water,[15] in contrast with the hydrophobic solute in aqueous solution, where the entropy term is superior to enthalpy term.[16] The values of TS^{ex} among three isomers decrease in the order D-glucose, D-mannose, and D-galactose.

To investigate the structural change of solvent water, excess partial molar quantities of water were calculated by the following equations.

$$\bar{G}_w^{ex} = mRT(1 - \phi)\frac{M_w}{1000}, \tag{5}$$

$$\bar{H}_w^{ex} = -(h_{xx}m^2 + 2h_{xxx}m^3)\frac{M_w}{1000}, \tag{6}$$

$$\bar{S}_w^{ex} = (\bar{H}_w^{ex} - \bar{G}_w^{ex})/T, \tag{7}$$

where $\bar{G}_w^{ex}$, $\bar{H}_w^{ex}$, and $\bar{S}_w^{ex}$ are the excess partial molar free energy, enthalpy, and entropy of water, respectively.

Table 1. Molalities of isopiestic solutions

D-Glucose

m(NaCl)[a]	m(Glucose)	m($CaCl_2$)[a]	m(Glucose)	m($CaCl_2$)[a]	m(Glucose)
0.1837	0.3384	0.2838	0.7930	1.1959	3.5996
0.3578	0.6520	0.4733	1.2547	1.2636	3.8538
0.4989	0.9026	0.5993	1.6166	1.3728	4.2811
0.5807	1.0484	0.6645	1.8094	1.4667	4.6536
0.6441	1.1608	0.7206	1.9878	1.5531	5.0090
0.7630	1.3725	0.7966	2.2282	1.6962	5.6249
0.8384	1.5040	0.8545	2.4122	1.7930	6.0510
0.9296	1.6634	0.9466	2.7181	1.8240	6.1977
1.0069	1.8009	1.0435	3.0489		
1.0919	1.9454	1.1447	3.4120		

D-Mannose

m(NaCl)[a]	m(Mannose)	m($CaCl_2$)[a]	m(Mannose)	m($CaCl_2$)[a]	m(Mannose)
0.2257	0.4160	0.4406	1.1849	1.5956	5.4166
0.4318	0.7927	0.5783	1.5953	1.6110	5.4839
0.4990	0.9162	0.6646	1.8657	1.6670	5.7387
0.5380	0.9884	0.7163	2.0324	1.6843	5.8187
0.5807	1.0662	0.8143	2.3533	1.8352	6.5255
0.7634	1.4026	0.9389	2.7913	1.8781	6.7322
0.8385	1.5416	0.9649	2.8800	1.8798	6.7401
0.8862	1.6242	1.0114	3.0481		
0.9296	1.7065	1.0574	3.2249		
1.0069	1.8496	1.1741	3.6670		
1.0911	2.0045	1.3558	4.3884		
1.3251	2.4375	1.4225	4.6767		

D-Galactose

m($CaCl_2$)[a]	m(Galactose)[a]	m($CaCl_2$)[a]	m(Galactose)
0.2532	0.6597	0.7687	2.1946
0.2973	0.7794	0.8352	2.4117
0.3855	1.0252	1.0180	3.0534
0.4839	1.3101	1.0733	3.2622
0.6381	1.7765	1.1246	3.4489
0.6843	1.9196		

a) The osmotic coefficients of standard solutions were obtained from the Appendix of "Electrolyte Solutions."[17]

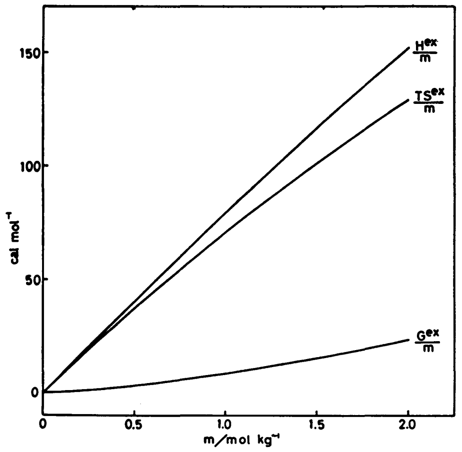

Fig. 1. Excess thermodynamic quantities for aqueous D-glucose solutions at 25 °C.

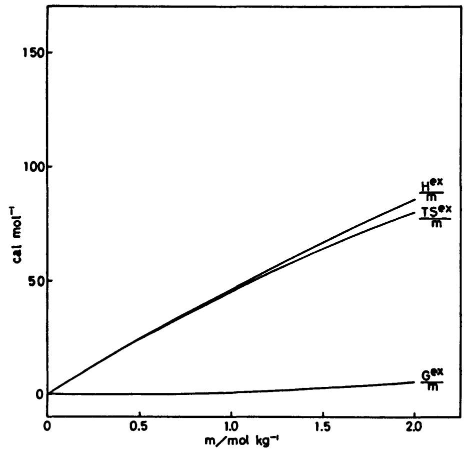

Fig. 2. Excess thermodynamic quantities for aqueous D-mannose solutions at 25 °C.

As shown in Fig. 4, the values of $\bar{S}^{\text{ex}}_{\text{w}}$ for D-glucose, D-mannose, and D-galactose are negative and the absolute values increase with concentration of monosaccharide, indicating the ordering of water molecule by the dissolution of these monosaccharides. As shown in Fig. 5, the predominance of enthalpy term over entropy term gives the negative value of $\bar{G}^{\text{ex}}_{\text{w}}$. The negative $\bar{S}^{\text{ex}}_{\text{w}}$ values which mean the increase of water structure lie in the order D-glucose>D-mannose>D-galactose. Tait[4] calculated the percentage of equatorial

Table 2. Osmotic and activity coefficients of hexoses at 25 °C

m	ϕ	γ	m	ϕ	γ	m	ϕ	γ
D-Glucose								
0.1	1.001	1.002	0.9	1.018	1.031	3.0	1.086	1.166
0.2	1.002	1.004	1.0	1.021	1.036	3.5	1.101	1.200
0.3	1.004	1.006	1.2	1.027	1.047	4.0	1.114	1.233
0.4	1.005	1.009	1.4	1.034	1.059	4.5	1.126	1.266
0.5	1.007	1.013	1.6	1.040	1.071	5.0	1.137	1.298
0.6	1.010	1.017	1.8	1.047	1.084	5.5	1.147	1.329
0.7	1.012	1.021	2.0	1.054	1.097	6.0	1.156	1.306
0.8	1.015	1.026	2.5	1.071	1.131			
D-Mannose								
0.1	1.000	1.000	0.9	1.004	1.005	3.0	1.043	1.068
0.2	1.000	1.000	1.0	1.005	1.006	3.5	1.055	1.088
0.3	1.000	1.000	1.2	1.007	1.010	4.0	1.066	1.109
0.4	1.000	1.000	1.4	1.010	1.014	4.5	1.076	1.130
0.5	1.001	1.001	1.6	1.014	1.019	5.0	1.085	1.150
0.6	1.001	1.001	1.8	1.017	1.025	5.5	1.094	1.169
0.7	1.002	1.002	2.0	1.021	1.031	6.0	1.101	1.189
0.8	1.003	1.003	2.5	1.032	1.048			
D-Galactose								
0.1	1.000	1.001	0.7	1.003	1.005	1.6	1.016	1.025
0.2	1.001	1.001	0.8	1.004	1.006	1.8	1.021	1.032
0.3	1.001	1.002	0.9	1.005	1.007	2.0	1.026	1.039
0.4	1.001	1.002	1.0	1.006	1.009	2.5	1.039	1.061
0.5	1.002	1.003	1.2	1.008	1.013	3.0	1.051	1.083
0.6	1.002	1.004	1.4	1.012	1.018	3.5	1.061	1.104

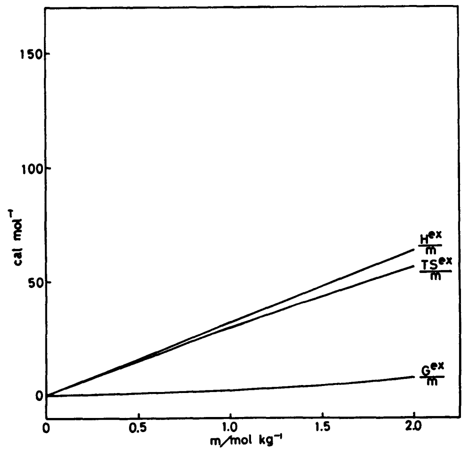

Fig. 3. Excess thermodynamic quantities for aqueous D-galactose solutions at 25 °C.

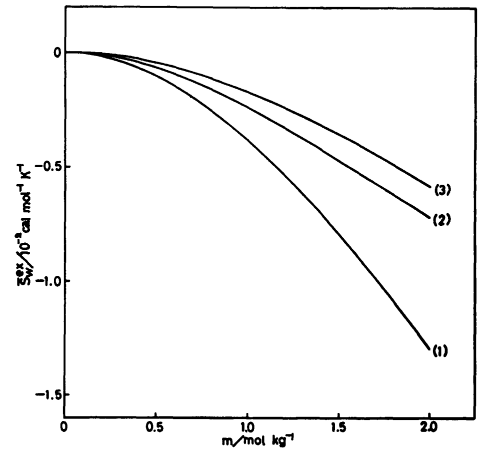

Fig. 4. Excess partial molar entropy of water ($\bar{S}_w^{ex}$) in aqueous D-glucose (1), D-mannose (2), and D-galactose (3) solutions at 25 °C.

OH groups of isomeric monosaccharides assuming that these monosaccharides take chair conformations and are the equilibrium mixtures of α- and β-anomers. Using his results, we calculated the equatorial OH content of D-galactose and D-mannose relative to D-glucose, resulting in 0.78 and 0.71 for D-galactose and D-mannose, respectively. Therefore the structure making ability must be in the order D-glucose>D-galactose>D-mannose. From the ^{17}O-NMR study,[4] Tait could not distinguish the hydration properties of three isomers and concluded that "at least three equatorial hydroxyl groups are required for the monosaccharide to be an effective substitute for the water within structured cluster of water molecules." Judging from the $\bar{S}_w^{ex}$ values of three isomers obtained from this work, the structure making ability lies in the order D-glucose>D-mannose>D-galactose. We cannot explain the discrepancy of structure making ability observed between our result and special hydration model at the present stage. A possible explanation is that the nature of structure promotion of these monosaccharides is affected not only by the number of equatorial hydroxyl groups but also by the relative position of equatorial hydroxyl groups,

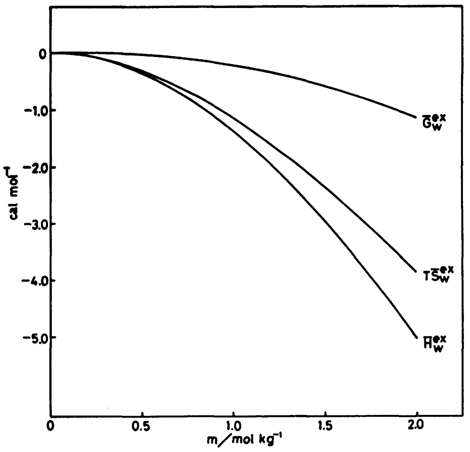

Fig. 5. Excess partial molar free energy, enthalpy, and entropy of water in aqueous D-glucose solutions at 25 °C.

on the assumption that the special hydration model is correct.

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