Ultrasonic and Densimetric Characterizations of the Hydration Properties of Polar Groups in Monosaccharides

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The partial molar volumes and adiabatic compressibilities for 14 monosaccharides in aqueous solution at the temperatures of 18, 25, 40, and 55 °C are reported. These experimental data allow estimation of the solvent contraction, V_I, caused by the polar groups of monosaccharides with four, five, and six polar groups. On average, each polar group in pentoses causes a 15−20% stronger contraction of water than a polar group in 2-deoxyribose, while each polar group in hexoses causes a 5−10% stronger contraction of water than a polar group in 2-deoxyhexoses and 6-deoxyhexoses. In addition, polar groups of 2-deoxyribose, 2-deoxyglucose, and 2-deoxygalactose exhibit essentially higher (less negative) compressibility contributions relative to polar groups of pentoses, 6-deoxyhexoses, and hexoses. The volume and compressibility data reported in this paper suggest similar hydration of the polar groups of pentoses and hexoses. Furthermore, the data suggest that, in monosaccharides, the hydroxyl group in the 2-position plays a crucial role in "switching on" the cooperative amplification of solute hydration (perhaps, via the formation of water networks). Removal of this group brings about a dramatic decrease in solute hydration with a concomitant increase in the compressibility contribution per polar group. Consequently, 2-deoxyribose and 2-deoxyhexoses manifest significantly weaker hydration compared to pentoses, 6-deoxyhexoses, and hexoses.

1. Introduction

Carbohydrates, consisting of an aliphatic moiety and polar hydroxyl groups, are appropriate models for studying hydration properties of proteins and nucleic acids. Consequently, in an attempt to gain a better understanding of the hydration of these biopolymers, a large number of solution studies of simple sugars have been conducted.[1−12] In particular, volumetric investigations have revealed strong stereochemical dependence of the hydration of monosaccharides.[9−14] Closely related stereoisomers of monosaccharides have been shown to exhibit vastly different values of partial molar volume and/or partial molar adiabatic compressibility. To account for this observation, it has been suggested that the hydration of each polar group in pentoses and hexoses depends on the relative position of that group with respect to the other polar groups.[11,12] Furthermore, it has been proposed[11,12] that when the distances between two or more hydroxyl oxygen atoms of a sugar match the second-nearest-neighbor distance of the oxygen atom in water molecules (4.82 Å) the overall hydration increases cooperatively. Such hydroxyl groups are believed to "fit" better into the tetrahedral structure of water. Significantly, these speculations are in accord with the results of volumetric studies of other organic compounds comprising polar groups (alcohols, amino acids, and oligopeptides). It has been shown that the hydration properties of a solute polar group strongly depend on the proximity of other polar groups.[15−19] When two or more polar groups are brought together in a solute molecule, hydration of each polar group additionally increases, as judged by a strong decrease in solute partial molar volume and partial molar adiabatic compressibility.[18]

These peculiarities of the hydration properties of polar groups were further underscored by the results of a recent volumetric study of globular proteins.[20] Specifically, based on volume and compressibility measurements, Chalikian et al.[20] found that, in globular proteins, each solvent-accessible polar group may influence the water of hydration 3 to 4 times more strongly than a corresponding polar group in small model compounds. As a working hypothesis, it was proposed that extensive water networks may form on protein surfaces with many closely located polar groups, thereby cooperatively enhancing protein hydration.[20]

In this work, the hydration properties of polar groups are further investigated. To this end, volumetric properties of 14 monosaccharides belonging to the family of D-aldoses with four to six polar groups have been systematically studied. For some of these monosaccharides, volumetric data have already been reported in the literature. However, most of the previous volumetric studies on simple sugars have been conducted only at a single temperature of 25 °C.[9−14] This seriously limits the usefulness of the published data, since hydration effects in solution are strongly sensitive to temperature. Consequently, temperature-dependent studies are required to develop a more complete understanding of hydration of carbohydrates. To fill this gap, in this paper, the partial molar volumes and the partial molar adiabatic compressibilities of four pentoses (ribose, arabinose, xylose, and lyxose), five hexoses (glucose, mannose, galactose, allose, and tallose), one 2-deoxypentose (2-deoxyribose), two 2-deoxyhexoses (2-deoxyglucose and 2-deoxygalactose), and two 6-deoxyhexoses (6-deoxyglucose and 6-deoxygalactose) are determined as a function of temperature. The resulting data are discussed in terms of the hydration properties of polar groups.

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2. Experimental Section

All monosaccharides used in this study were of the highest purity commercially available and were used without further purification. Specifically, 2-deoxy-D-ribose, D-ribose, D-arabinose, D-xylose, D-lyxose, 6-deoxy-D-glucose, D-glucose, D-mannose, and D-galactose were purchased from Fluka (Buchs, Switzerland), 2-deoxy-D-glucose, 2-deoxy-D-galactose, D-allose, and D-talose were purchased from ICN Biomedicals (Costa Mesa, CA), while 6-deoxy-D-galactose was obtained from Sigma Chemical (St. Louis, MO).

Solutions of monosaccharides were prepared with triply distilled water, which was degassed by boiling. The concentration of each sample was determined by weighing 10−20 mg of solute with a precision of ±0.03 mg and dissolving in a known amount of water. All monosaccharides were dried under vacuum in the presence of phosphorus pentoxide for 5 days prior to weighing. To prevent formation of air bubbles, all solutions were preheated to 5 °C above the measuring temperature before placing them into the ultrasonic or densimetric cells.

All densities were measured by using a vibrating tube densimeter (DMA-60, Anton Paar, Austria) with a precision of $\pm 1.5 \times 10^{-6}$ g/cm^3 at 18, 25, 40, and 55 °C. The apparent molar volume, ϕV, was calculated from the standard equation:

$$\phi V = M/\rho - (\rho - \rho_0)/(\rho_0 \rho m) \quad (1)$$

where M is the molecular weight of the solute, m is the molal concentration, and ρ and ρ_0 are the densities of the solution and solvent, respectively. Values for the density of water were taken from the work of Kell.[21]

The solution sound velocity values, required to calculate the apparent molar adiabatic compressibility, ϕK_S, of a solute were measured with a precision of $\pm 2 \times 10^{-4}$% at 18, 25, 40, and 55 °C, using the resonator method[22−26] at a frequency of about 7.5 MHz. Ultrasonic resonator cells with sample volumes of 0.8 cm^3 were thermostated with an accuracy of ±0.01 °C, and a previously described differential technique was employed for all measurements.[23]

Apparent molar adiabatic compressibility values for the solutes were calculated from the densimetric and ultrasonic data by using the expression:[27]

$$\phi K_S = \beta_{S0} (2\phi V - 2[U] - M/\rho_0) \quad (2)$$

where β_{S0} is the coefficient of adiabatic compressibility of water, $[U]$ is the relative molar sound velocity increment of a solute and is equal to $(U - U_0)/(U_0 C)$, U and U_0 are the sound velocities in the solution and solvent, respectively, and C is the molar concentration. The coefficient of adiabatic compressibility of water, β_{S0}, required to evaluate ϕK_S from eq 2 was calculated from the data on density[21] and sound velocity,[28] since $\beta_{S0} = (\rho_0 U_0^2)^{-1}$.

For each evaluation of ϕV or ϕK_S, three to four independent measurements were carried out at a concentration of about 3 mg/mL for all of the carbohydrates.

3. Results

Tables 1, 2 and 3 show the relative molar sound velocity increments, $[U]$, apparent molar volumes, ϕV, and apparent molar adiabatic compressibilities, ϕK_S, for the 14 monosaccharides measured at 18, 25, 40, and 55 °C, respectively. Errors were estimated by summing the maximum uncertainties due to concentration determination, temperature drift, and apparatus limitation. The concentration dependencies of the apparent molar volume and compressibility of all monosaccharides are known to be negligible at the concentrations used in the present work.[10,11,13,14] Within the limits of the experimental error, the apparent molar volumes, ϕV, and adiabatic compressibilities, ϕK_S, determined at a concentration of 3 mg/mL coincide with the partial molar volumes, $V°$, and adiabatic compressibilities, $K°_S$, obtained by extrapolation to infinite dilution. Thus, below,

TABLE 1: Relative Molar Sound Velocity Increments, [*U*] (cm^3 mol^{-1}), as a Function of Temperature, *T*, for the Monosaccharides[a]

	18 °C	25 °C	40 °C	55 °C
2-deoxyribose	36.8 ± 0.2	33.3 ± 0.2	27.3 ± 0.3	22.1 ± 0.3
ribose	38.4 ± 0.2	34.3 ± 0.2	28.3 ± 0.3	24.3 ± 0.3
arabinose	43.7 ± 0.2	40.5 ± 0.2	35.1 ± 0.3	30.4 ± 0.3
xylose	38.4 ± 0.2	35.0 ± 0.2	29.2 ± 0.3	25.5 ± 0.3
lyxose	36.8 ± 0.2	34.3 ± 0.2	28.7 ± 0.3	24.6 ± 0.3
2-deoxyglucose	38.5 ± 0.2	35.4 ± 0.2	29.6 ± 0.3	25.1 ± 0.3
2-deoxygalactose	40.4 ± 0.2	37.5 ± 0.2	31.5 ± 0.3	26.5 ± 0.3
6-deoxyglucose	49.8 ± 0.2	45.6 ± 0.2	37.6 ± 0.3	31.7 ± 0.3
6-deoxygalactose	55.1 ± 0.2	50.3 ± 0.2	40.9 ± 0.3	33.6 ± 0.3
glucose	45.4 ± 0.2	42.1 ± 0.2	35.9 ± 0.3	32.2 ± 0.3
mannose	41.3 ± 0.2	37.8 ± 0.2	34.0 ± 0.3	31.7 ± 0.3
galactose	46.3 ± 0.2	43.5 ± 0.2	38.3 ± 0.3	34.6 ± 0.3
allose	47.3 ± 0.2	43.7 ± 0.2	37.9 ± 0.3	34.2 ± 0.3
talose	38.9 ± 0.2	35.4 ± 0.2	29.5 ± 0.3	26.8 ± 0.3

[a] Errors are estimated by summing the maximum uncertainties due to concentration determination, temperature drift, and apparatus limitation.

TABLE 2: Partial Molar Volumes, $V°$ (cm^3 mol^{-1}), as a Function of Temperature, *T*, for the Monosaccharides[a]

	18 °C	25 °C	40 °C	55 °C
2-deoxyribose	93.8 ± 0.3	94.2 ± 0.3	95.2 ± 0.4	96.7 ± 0.5
ribose	94.0 ± 0.3	95.0 ± 0.3	96.9 ± 0.4	97.8 ± 0.5
arabinose	91.5 ± 0.3	92.2 ± 0.3	94.0 ± 0.4	95.8 ± 0.5
xylose	94.5 ± 0.3	95.0 ± 03	96.3 ± 0.4	96.8 ± 0.5
lyxose	92.5 ± 0.3	93.6 ± 0.3	95.6 ± 0.4	96.5 ± 0.5
2-deoxyglucose	112.2 ± 0.3	112.6 ± 0.3	114.0 ± 0.4	114.9 ± 0.5
2-deoxygalactose	110.0 ± 0.3	110.5 ± 0.3	112.0 ± 0.3	113.0 ± 0.5
6-deoxyglucose	110.0 ± 0.3	110.7 ± 0.3	112.6 ± 0.3	113.9 ± 0.5
6-deoxygalactose	108.3 ± 0.3	108.8 ± 0.3	110.3 ± 0.3	111.7 ± 0.5
glucose	109.8 ± 0.3	110.9 ± 0.3	112.8 ± 0.4	114.0 ± 05
mannose	109.5± 0.3	111.1 ± 0.3	112.5 ± 0.4	113.7 ± 0.5
galactose	109.0 ± 0.3	109.8 ± 0.3	111.3 ± 0.4	112.3 ± 0.5
allose	109.6 ± 0.3	110.0 ± 0.3	111.7 ± 0.4	113.4 ± 0.5
talose	111.0 ± 0.3	111.6 ± 0.3	113.1 ± 0.4	114.4 ± 0.5

[a] Errors are estimated by summing the maximum uncertainties due to concentration determination, temperature drift, and apparatus limitation.

TABLE 3: Partial Molar Adiabatic Compressibilities, $K°_S$ (10^{-4} cm^3 mol^{-1} bar^{-1}), as a Function of Temperature, *T*, for the Monosaccharides[a]

	18 °C	25 °C	40 °C	55 °C
2-deoxyribose	−9.3 ± 0.5	−5.7 ± 0.5	0.3 ± 0.6	5.6 ± 0.7
ribose	−18.0 ± 0.5	−13.1 ± 0.5	−6.1 ± 0.6	−2.2 ± 0.7
arabinose	−25.2 ± 0.5	−21.1 ± 0.5	−14.4 ± 0.6	−9.1 ± 0.7
xylose	−17.5 ± 0.5	−13.7 ± 0.5	−7.4 ± 0.6	−4.1 ± 0.7
lyxose	−17.9 ± 0.5	−14.3 ± 0.5	−7.5 ± 0.6	−3.6 ± 0.7
2-deoxyglucose	−7.8 ± 0.5	−4.6 ± 0.5	1.4 ± 0.6	5.5 ± 0.7
2-deoxygalactose	−11.6 ± 0.5	−8.3 ± 0.5	−1.9 ± 0.6	2.7 ± 0.7
6-deoxyglucose	−20.2 ± 0.5	−15.4 ± 0.5	−6.7 ± 0.6	−0.9 ± 0.7
6-deoxygalactose	−26.2 ± 0.5	−21.4 ± 0.5	−11.5 ± 0.6	−4.4 ± 0.7
glucose	−23.7 ± 0.5	−19.3 ± 0.5	−12.0 ± 0.6	−8.1 ± 0.7
mannose	−20.2 ± 0.5	−15.2 ± 0.5	−10.7 ± 0.6	−8.0 ± 0.7
galactose	−25.3 ± 0.5	−21.5 ± 0.5	−15.3 ± 0.6	−11.6 ± 0.7
allose	−25.7 ± 0.5	−21.5 ± 0.5	−14.7 ± 0.6	−10.3 ± 0.7
talose	−16.6 ± 0.5	−12.7 ± 0.5	−6.2 ± 0.6	−3.2 ± 0.7

[a] Errors are estimated by summing the maximum uncertainties due to concentration determination, temperature drift, and apparatus limitation.

the apparent molar and partial molar characteristics of the monosaccharides will be treated as equivalent.

Comparison of our data on $V°$ and $K°_S$ for the monosaccharides obtained at 25 °C and those reported in the literature[9−14] reveals reasonably good agreement.

4. Discussion

4.1 Partial Molar Volume. The partial molar volume of a solute at infinite dilution, $V°$, can be presented as the sum[17,29,30]

$$V° = V_M + V_T + V_I + \beta_{T0}RT \quad (3)$$

where V_M is the intrinsic volume of a solute molecule itself (for low molecular weight substances, the value of V_M can be approximated by the van der Waals volume, V_W); V_T is the "thermal" volume (the volume of the void space surrounding the solute molecule[30]), which is due to the thermally induced mutual molecular vibrations of the solute and the solvent; V_I is the "interaction volume", which represents a decrease in solvent volume (solvent contraction) resulting from hydration of polar or charged atomic groups of a solute; β_{T0} is the coefficient of isothermal compressibility of the solvent; R is the universal gas constant; and T is the absolute temperature. The term $\beta_{T0}RT$ describes the volume effect related to the kinetic contribution to the pressure of a solute molecule due to translational degrees of freedom.[31] The $\beta_{T0}RT$ term is small and only slowly increases with temperature (from 1.12 cm^3 mol^{-1} at 10 °C to 1.23 cm^3 mol^{-1} at 60 °C).

It can be shown that the thermal volume, V_T, of low molecular weight solutes is a linear function of the solvent-accessible surface area, S_A:[17,32]

$$V_T = AS_A + B \quad (4)$$

For small solutes, the solvent-accessible surface area, S_A, can be approximated by the van der Waals surface area, S_W. The coefficient B in eq 4 represents the thermal volume created by a point particle and can be estimated based on concepts of the scaled particle theory (SPT).[29] For aqueous solutions, the value of B is about 0.6 cm^3 mol^{-1} and does not strongly depend on temperature within the 10−60 °C range.

The coefficient A in eq 4 has been determined for homologous series of α,ω-aminocarboxylic acids at 18, 25, 40, and 55 °C,[32] diglycyl tripeptides with nonpolar side chains at 25 °C,[33] α-amino acids at 25 and 55 °C,[17] and hydrocarbons at 25 °C (Chalikian, T. *V.*, unpublished data). It should be noted that the values of A practically coincide for these very different compounds. For instance, at 25 °C, the value of A for α,ω-aminocarboxylic acids, diglycyl tripeptides, α-amino acids, and hydrocarbons is equal to 4.05×10^{-9}, 4.20×10^{-9}, 4.13×10^{-9}, and 4.21×10^{-9} cm, respectively. Below, the values of A, which were obtained for α,ω-aminocarboxylic acids[32] will be used to calculate the thermal volume, V_T, of the monosaccharides.

The interaction volume, V_I, represents the reduction of solvent volume due to the hydration of the polar groups of monosaccharides. The values of V_I calculated using eqs 3 and 4 are listed in Table 4. The intrinsic volumes, V_M, of the molecules and their solvent accessible surface areas, S_A, necessary for these calculations were determined by using the additive approach of Bondi.[34] For 2-deoxyribose, pentoses, 2- and 6-deoxyhexoses, and hexoses, S_A is equal to 9.53×10^9 cm^2 mol^{-1} (158.3 Å^2), 10.2×10^9 cm^2 mol^{-1} (169.5 Å^2), 11.53×10^9 cm^2 mol^{-1} (192.1 Å^2), and 12.2×10^9 cm^2 mol^{-1} (203.3 Å^2), respectively. For 2-deoxyribose, pentoses, 2- and 6-deoxihexoses, and hexoses, V_M is equal to 70.1 cm^3 mol^{-1} (116.4 Å^3), 74.7 cm^3 mol^{-1} (124.0 Å^3), 84.9 cm^3 mol^{-1} (141.0 Å^3), and 89.5 cm^3 mol^{-1} (148.6 Å^3), respectively.

TABLE 4: Interaction Volumes, V_I (cm^3 mol^{-1}), as a Function of Temperature, T, for the Monosaccharides[a]

	18 °C	25 °C	40 °C	55 °C
2-deoxyribose	−14.8 ± 0.3	−16.2 ± 0.3	−16.6 ± 0.4	−18.4 ± 0.5
ribose	−21.9 ± 0.3	−22.8 ± 0.3	−22.3 ± 0.4	−25.0 ± 0.5
arabinose	−24.4 ± 0.3	−25.6 ± 0.3	−25.2 ± 0.4	−27.0 ± 0.5
xylose	−21.4 ± 0.3	−22.8 ± 0.3	−23.6 ± 0.4	−26.0 ± 0.5
lyxose	−23.4 ± 0.3	−24.2 ± 0.3	−23.6 ± 0.4	−26.3 ± 0.5
2-deoxyglucose	−19.0 ± 0.3	−20.7 ± 0.3	−21.0 ± 0.4	−24.2 ± 0.5
2-deoxygalactose	−21.2 ± 0.3	−22.8 ± 0.3	−22.9 ± 0.4	−26.1 ± 0.5
6-deoxyglucose	−21.2 ± 0.3	−22.6 ± 0.3	−22.4 ± 0.4	−25.2 ± 0.5
6-deoxygalactose	−22.9 ± 0.3	−24.5 ± 0.3	−24.7 ± 0.4	−27.4 ± 0.5
glucose	−28.8 ± 0.3	−29.9 ± 0.3	−29.7 ± 0.4	−32.8 ± 0.5
mannose	−29.1 ± 0.3	−29.7 ± 0.3	−30.0 ± 0.4	−33.1 ± 0.5
galactose	−29.6 ± 0.3	−31.0 ± 0.3	−31.2 ± 0.4	−34.5 ± 0.5
allose	−29.0 ± 0.3	−30.8 ± 0.3	−30.8 ± 0.4	−33.4 ± 0.5
talose	−27.6 ± 0.3	−29.2 ± 0.3	−29.4 ± 0.4	−32.4 ± 0.5

[a] Errors are taken equal to those for the partial molar volume data presented in Table 2.

TABLE 5: Average Interaction Volumes Per Polar Group, V_I (cm^3 mol^{-1}), as a Function of Temperature, T, for the Different Classes of Monosaccharides[a]

	18 °C	25 °C	40 °C	55 °C
2-deoxypentose[b]	−3.7 ± 0.2	−4.1 ± 0.2	−4.2 ± 0.2	−4.6 ± 0.2
pentoses	−4.6 ± 0.2	−4.8 ± 0.2	−4.7 ± 0.2	−5.2 ± 0.2
2-deoxyhexoses	−4.0 ± 0.2	−4.4 ± 0.2	−4.4 ± 0.2	−5.0 ± 0.2
6-deoxyhexoses	−4.4 ± 0.2	−4.7 ± 0.3	−4.7 ± 0.2	−5.3 ± 0.2
hexoses	−4.8 ± 0.1	−5.0 ± 0.1	−5.1 ± 0.2	−5.5 ± 0.2

[b] Errors are calculated as standard deviations of the mean. [b] Errors for 2-deoxyribose are taken equal to those for pentoses.

Inspection of Table 4 reveals that, in agreement with conventional wisdom, V_I decreases when the number of polar groups within a solute increases. Note that, for each class of monosaccharides (pentoses, hexoses, etc.), V_I is remarkably constant within the limits of ±5%. For instance, for pentoses, at 25 °C, V_I ranges from −25.6 cm^3 mol^{-1} (arabinose) to −22.8 cm^3 mol^{-1} (ribose and xylose), while for hexoses, at 25 °C, V_I ranges from −31.0 cm^3 mol^{-1} (galactose) to −29.2 cm^3 mol^{-1} (talose). The observed similarity suggests that, within each class of monosaccharides (pentoses, hexoses, etc.), the contraction of water caused by each polar group is more or less the same. On average, at 25 °C, the values of V_I for pentoses and hexoses are equal to −24.0 ± 0.8 and −30.0 ± 0.5 cm^3 mol^{-1}, respectively. The difference between these values yields the apparent V_I contribution of a single hydroxyl group, which is equal to −6.0 ± 1.3 cm^3 mol^{-1}.

Comparison of the 2-deoxyribose and ribose V_I values (see Table 4) reveals that the removal of a hydroxyl group in pentoses results in an increase in V_I (At 25 °C, this increase is equal to 6.6 cm^3 mol^{-1}). Furthermore, comparison of the V_I values for 2- and 6-deoxyhexoses with those for glucose and galactose reveals that the removal of a hydroxyl group in hexoses causes an increase in V_I which, at 25 °C, ranges from 6.8 to 9.2 cm^3 mol^{-1} (on average, 7.9 ± 0.8 cm^3 mol^{-1}). It should be also noted that 2-deoxyhexoses are characterized by values of V_I which are only slightly higher (on the order of 1 to 2 cm^3 mol^{-1}) than those for 6-deoxyhexoses. This observation suggests that the volume observable is not very sensitive to the differential hydration of these isomers.

Table 5 shows the average values of V_I per polar group (V_I divided by the number of polar groups in a monosaccharide) for the different monosaccharides used in this study [2-deoxy-

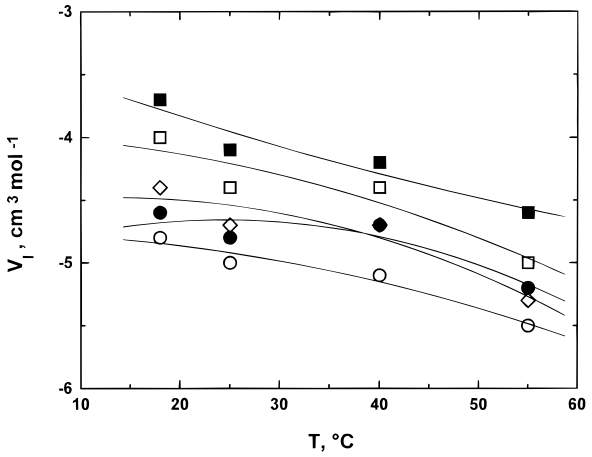

Figure 1. Temperature dependencies of the average solvent contractions, V_I, per polar group for 2-deoxyribose (■), pentoses (●), 2-deoxyhexoses (□), 6-deoxyhexoses (◇), and hexoses (○).

pentose (2-deoxyribose), pentoses, 2-deoxyhexoses, 6-deoxyhexoses, and hexoses]. Note that the values of V_I per polar group for these monosaccharides are within range of similar estimates for V_I per polar group for other organic compounds.[30] The numbers given in Table 5 are slightly less negative than the estimate of V_I per hydroxyl group -6.0 cm^3 mol^{-1} arrived at by subtracting the average value of V_I for pentoses from that for hexoses. This discrepancy may reflect the fact that, in monosaccharides, the ring oxygen is somewhat less hydrated than each of the hydroxyl groups.[35]

The V_I data listed in Table 5 are graphically presented in Figure 1. Note that, for all five classes of monosaccharides (2-deoxypentoses, pentoses, 2-deoxyhexoses, 6-deoxyhexoses, and hexoses), the V_I per polar group decreases when temperature increases. For instance, for hexoses, the V_I per polar group decreases from -4.8 cm^3 mol^{-1} at 18 °C to -5.5 cm^3 mol^{-1} at 55 °C.

Inspection of Figure 1 reveals the following two features: (i) At all temperatures studied, the average value of V_I per polar group for 2-deoxyribose (-4.1 cm^3 mol^{-1} at 25 °C) is 15−20% smaller than that for pentoses (-4.8 cm^3 mol^{-1} at 25 °C). This disparity reflects stronger hydration of the polar groups of pentoses relative to those of 2-deoxyribose. Similarly, the average V_I per polar group for 2-deoxyhexoses (-4.4 cm^3 mol^{-1} at 25 °C) and 6-deoxyhexoses (-4.7 cm^3 mol^{-1} at 25 °C) is 5−10% smaller than that for hexoses (-5.0 cm^3 mol^{-1} at 25 °C), reflecting stronger hydration of the polar groups of hexoses relative to those of 2-deoxyhexoses and 6-deoxyhexoses. Within the framework of the volumetric observables used in this study, stronger hydration indicates either stronger solute−solvent hydrogen bonding or more waters affected by each polar group. (ii) Within experimental error, there is no difference in the magnitude of the V_I per polar group between hexoses and pentoses. Hence, the volume observable does not suggest any significant differences in the hydration of polar groups of hexoses and pentoses.

4.2. Partial Molar Adiabatic Compressibility. The partial molar adiabatic compressibility, $K°_S$, of a solute can be described as the sum of intrinsic and hydration contributions:[15]

$$K°_S = K_M + \Delta K_h = K_M + n_h(K_h - K_{S0}) \qquad (5)$$

where K_M is the intrinsic compressibility of a solute molecule, ΔK_h is the compressibility effect of hydration, K_{S0} and K_h are the partial molar adiabatic compressibilities of water in the bulk state and in the hydration shell of a solute, respectively, and

TABLE 6: Compressibility Contributions of Hydrophobic Groups, K_{hyd} (10^{-4} cm^3 mol^{-1} bar^{-1}), as a Function of Temperature, T, for the Different Classes of Monosaccharides

	18 °C	25 °C	40 °C	55 °C
deoxypentoses	−10.8	−5.3	3.9	9.4
pentoses	−8.9	−4.4	3.2	6.7
deoxyhexoses	−12.2	−5.9	4.4	10.7
hexoses	−10.3	−5.1	3.7	8.9

n_h, the hydration number, is the number of water molecules in the hydration shell of a solute.

For low molecular weight compounds, the intrinsic compressibility, K_M, is small since it is mostly determined by the compressibility of covalent bonds and external electron shells. Therefore, for small molecules including monosaccharides, the intrinsic term K_M in eq 5 can be neglected.[15] Consequently, the partial molar adiabatic compressibility of a monosaccharide predominantly reflects the hydration properties of its polar and aliphatic moieties. The hydration contribution of aliphatic groups to ΔK_h depends on the temperature; it is negative below 30 °C and becomes positive at higher temperatures.[15,18,32] The hydration contribution of polar groups to ΔK_h can be either positive or negative depending on the temperature and the proximity of other polar groups.[15,18]

In many cases, for partial molar adiabatic compressibilities of low molecular weight compounds, the additivity principle holds.[14,15,18,36] In other words, the value of $K°_S$ for a small solute can be calculated as the sum of hydration contributions of its constituent atomic groups. However, inspection of Table 3 reveals that, for monosaccharides, the additivity principle does not hold: molecules of the same chemical composition often exhibit different values of $K°_S$ (e.g., compare the pentoses arabinose and ribose or the hexoses galactose and talose). In agreement with previous studies, one may propose that differential hydration of isomeric monosaccharides predominantly arises from differential hydration of polar rather than nonpolar moieties.[10,11] In other words, monosaccharides of identical chemical composition should exhibit similar hydration of the hydrophobic groups, while the hydration of the polar groups may be quite different.

In monosaccharides, the compressibility contribution of aliphatic groups can be calculated if one assumes that 1 Å^2 of the solvent accessible hydrophobic surface of monosaccharides has the same compressibility contribution as 1 Å^2 of the $-CH_2-$ methylene group in a nonbranched aliphatic chain, e.g., in α,ω-aminocarboxylic acids.[32] The solvent accessible hydrophobic surface areas, S_{hyd}, of monosaccharides can be calculated according to Bondi.[34] For 2-deoxyribose, pentoses, 2- and 6-deoxyhexoses, and hexoses, S_{hyd} is equal to 73.1, 60.3, 82.5, and 69.7 Å^2, respectively, while the solvent accessible surface area of a $-CH_2-$ group is equal to 22.4 Å^2. Table 6 shows the estimated values of the hydrophobic compressibility contributions, K_{hyd}, for the monosaccharides. Using these data, the compressibility contributions of polar groups, K_{pol}, for the monosaccharides can be calculated by subtracting the hydrophobic contribution, K_{hyd}, from the partial molar adiabatic compressibility, $K°_S$ (see Table 7).

Inspection of Table 7 reveals that, in contrast to the interaction volume V_I (see Table 5), the compressibility contributions of polar groups, K_{pol}, may differ significantly within a given class of monosaccharides (e.g., pentoses, hexoses, etc.). For example, K_{pol} for pentoses, ranges from -16.7×10^{-4} cm^3 mol^{-1} bar^{-1} (arabinose) to -8.7×10^{-4} cm^3 mol^{-1} bar^{-1} (ribose) at 25 °C. For hexoses, K_{pol} ranges from -16.4×10^{-4} cm^3 mol^{-1} bar^{-1}

TABLE 7: Compressibility Contributions of Polar Groups, K_{pol} (10^{-4} cm^3 mol^{-1} bar^{-1}), as a Function of Temperature, T, for the Monosaccharides[a]

	18 °C	25 °C	40 °C	55 °C
2-deoxyribose	1.5 ± 0.5	−0.4 ± 0.5	−1.6 ± 0.6	−3.8 ± 0.7
ribose	−9.1 ± 0.5	−8.7 ± 0.5	−9.3 ± 0.6	−8.9 ± 0.7
arabinose	−16.3 ± 0.5	−16.7 ± 0.5	−17.6 ± 0.6	−15.8 ± 0.7
xylose	−8.6 ± 0.5	−9.3 ± 0.5	−10.6 ± 0.6	−10.8 ± 0.7
lyxose	−9.0 ± 0.5	−9.9 ± 0.5	−10.7 ± 0.6	−10.3 ± 0.7
2-deoxyglucose	4.4 ± 0.5	1.3 ± 0.5	−3.0 ± 0.6	−5.2 ± 0.7
2-deoxygalactose	0.6 ± 0.5	−2.4 ± 0.5	−6.3 ± 0.6	−8.0 ± 0.7
6-deoxyglucose	−8.0 ± 0.5	−9.5 ± 0.5	−11.1 ± 0.6	−11.6 ± 0.7
6-deoxygalactose	−14.0 ± 0.5	−15.5 ± 0.5	−15.9 ± 0.6	−15.1 ± 0.7
glucose	−13.4 ± 0.5	−14.2 ± 0.5	−15.7 ± 0.6	−17.0 ± 0.7
mannose	−9.9 ± 0.5	−10.1 ± 0.5	−14.4 ± 0.6	−16.9 ± 0.7
galactose	−15.0 ± 0.5	−16.4 ± 0.5	−19.0 ± 0.6	−20.5 ± 0.7
allose	−15.4 ± 0.5	−16.4 ± 0.5	−18.4 ± 0.6	−19.2 ± 0.7
talose	−6.3 ± 0.5	−7.6 ± 0.5	−9.9 ± 0.6	−12.1 ± 0.7

[a] Errors are taken equal to those for the partial molar adiabatic compressibility data presented in Table 3.

TABLE 8: Average Compressibility Contributions Per Polar Group, K_{pol} (10^{-4} cm^3 mol^{-1} bar^{-1}), as a Function of Temperature, T, for the Different Classes of Monosaccharides[a]

	18 °C	25 °C	40 °C	55 °C
2-deoxypentose[b]	0.4 ± 0.8	−0.1 ± 0.8	−0.4 ± 0.8	−1.0 ± 0.7
pentoses	−2.2 ± 0.8	−2.2 ± 0.8	−2.4 ± 0.8	−2.3 ± 0.7
2-deoxyhexoses	0.5 ± 0.4	−0.1 ± 0.4	−0.9 ± 0.4	−1.3 ± 0.3
6-deoxyhexoses	−2.2 ± 0.6	−2.5 ± 0.7	−2.7 ± 0.5	−2.7 ± 0.4
hexoses	−2.0 ± 0.8	−2.2 ± 0.8	−2.6 ± 0.8	−2.8 ± 0.7

[a] Errors are calculated as standard deviations of the mean. [b] Errors for 2-deoxyribose are taken equal to those for pentoses.

(galactose) to -7.6×10^{-4} cm^3 mol^{-1} bar^{-1} (talose) at 25 °C. Also, note that there are very large differences in the values of K_{pol} for isomeric 2- and 6-deoxyhexoses. At all temperatures studied, 2-deoxyglucose and 2-deoxygalactose exhibit significantly higher (less negative) values of K_{pol} than do 6-deoxyglucose and 6-deoxygalactose (e.g., at 25 °C, on average, this difference is as large as 10.8×10^{-4} cm^3 mol^{-1} bar^{-1}). As will be elaborated on below, this observation can be rationalized in terms of stronger hydration of 6-deoxyhexoses relative to their isomeric 2-deoxyhexose counterparts.

There are two possible scenarios which can be proposed to address the observed large negative values of K_{pol} for some carbohydrates (e.g., arabinose): (i) a cooperative enhancement of hydration, involving all polar groups of these carbohydrates occurs, and (ii) only some polar groups (not all) exhibit unusually strong hydration. In the first scenario, the compressibility contributions of all polar groups of the molecule are more or less equal. By contrast, in the second scenario, some polar groups may exhibit very low compressibility contributions by far exceeding the contributions from other polar groups. Reliable discrimination between these two scenarios of sugar hydration is complicated since, in solutions, sugars do not assume a single conformational state but rather exist as multiple stereoisomeric conformers. Under equilibrium conditions, monosaccharides exist as mixtures of two or more anomers and/or tautomers with the proportions depending on temperature, concentration, and the nature of the solvent.[4,5] Therefore, below, the average values of K_{pol} per polar group are calculated by using the simplest assumption that all polar groups of a molecule have similar compressibility contributions.

Table 8 shows the average values of K_{pol} per polar group for monosaccharides with four, five, and six polar groups (K_{pol} divided by the number of polar groups). However, as discussed above, one cannot exclude the possibility that the compressibility contributions of individual polar groups of monosaccharides may differ from those presented in Table 8.

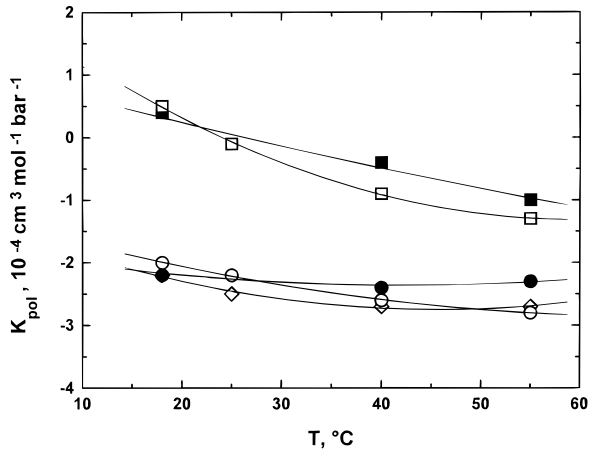

Figure 2. Temperature dependencies of the average compressibility contributions per polar group for 2-deoxyribose (■), pentoses (●), 2-deoxyhexoses (□), 6-deoxyhexoses (◇), and hexoses (○).

The K_{pol} data listed in Table 8 are graphically presented in Figure 2, inspection of which reveals the following four important observations:

(i) Within experimental error, each polar group of pentoses and hexoses contributes to a similar extent to the partial compressibility. For example, at 25 °C, the average compressibility contribution of a polar group for both pentoses and hexoses is equal to $-(2.2 \pm 0.8) \times 10^{-4}$ cm^3 mol^{-1} bar^{-1}. Thus, both volume and compressibility observables suggest similar hydration of the polar groups of pentoses and hexoses.

(ii) The value of K_{pol} per polar group for 6-deoxyhexoses (equal to -2.5×10^{-4} cm^3 mol^{-1} bar^{-1} at 25 °C) is close to that for pentoses and hexoses. Therefore, one can reasonably propose that the pattern of hydration of polar groups of 6-deoxyhexoses does not significantly differ from that of polar groups of pentoses and hexoses.

(iii) 2-Deoxyribose and 2-deoxyhexoses exhibit rather similar values of K_{pol} per polar group (equal to -0.1×10^{-4} cm^3 mol^{-1} bar^{-1} at 25 °C). This observation is consistent with a similar pattern of hydration of polar groups of 2-deoxyribose and 2-deoxyhexoses.

(iv) Polar groups of 2-deoxyribose, 2-deoxyglucose, and 2-deoxygalactose exhibit essentially higher (less negative) compressibility contribution relative to polar groups of pentoses, 6-deoxyhexoses, and hexoses. This observation is consistent with the polar groups of pentoses, 6-deoxyhexoses, and hexoses being essentially more strongly hydrated than those of 2-deoxyribose, 2-deoxyglucose, and 2-deoxygalactose. To account for this differential hydration, it can be proposed that, in monosaccharides, the hydroxyl group in the 2-position plays a crucial role in "switching on" the cooperative amplification of the solute hydration (perhaps, via the formation of water networks). Consequently, removal of this group should bring about a dramatic decrease in the solute hydration with a concomitant increase in K_{pol} per polar atom. Other hydroxyl groups (such as 6-hydroxyl group in glucose and galactose) may play a more modest role in the formation of the cooperative structure of the hydration shell of pentoses and hexoses.

However, recall that ribose, glucose, and galactose all have an equatorial hydroxyl group in the 2-position.[11] Since it was argued that sugar hydration may depend on the relative position of its axial and equatorial groups,[11] one cannot exclude the possibility that in pentoses and hexoses with an axial hydroxyl

group in the 2-position (such as lyxose, mannose, or talose) the hydration can be dominated by other polar groups. Further studies are required to prove or refute the generality of the discussions and conclusions presented above.

5. Concluding Remarks

This paper reports the partial molar volumes and adiabatic compressibilities for 14 monosaccharides in aqueous solution within the temperature range of 18−55 °C. Based on these data, the solvent contraction, V_I, caused by polar groups of monosaccharides with four, five, and six polar groups have been estimated. On average, each polar group in pentoses causes a 15−20% stronger contraction of water than a polar group in 2-deoxyribose, while each polar group in hexoses causes a 5−10% stronger contraction of water than a polar group in 2-deoxyhexoses and 6-deoxyhexoses.

In addition, the compressibility contributions of polar groups of the monosaccharides have been evaluated. Polar groups of 2-deoxyribose and 2-deoxyhexoses exhibit essentially higher (less negative) compressibility contributions relative to polar groups of pentoses, 6-deoxyhexoses, and hexoses. By contrast, the hydration of polar groups of pentoses and hexoses is similar as can be judged by the volume and compressibility observables. Furthermore, the volumetric results presented in this paper suggest that, in pentoses and hexoses, the hydroxyl group in the 2-position plays a crucial role in "switching on" the cooperative amplification of solute hydration (perhaps, via the formation of water networks). Removal of this group brings about a dramatic decrease in solute hydration with a concomitant increase in the compressibility contribution per polar group. Consequently, 2-deoxyribose and 2-deoxyhexoses manifest significantly weaker hydration compared to pentoses, 6-deoxyhexoses, and hexoses.

In the aggregate, independent of the veracity of these interpretations, the volumetric data reported here provide a quantitative description of the hydration properties of polar groups which should prove useful in understanding the role of solvent in the stabilization/destabilization of biologically relevant macromolecules and their complexes.

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