Determination of the Specific Heat Capacities of Aqueous Solutions of Pentose

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A laboratory-constructed isoperibol twin calorimeter of dry shield type (*J. Chem. Thermodyn.*, **13**, 89 (1981)) was used for measurements of the specific heat capacities of aqueous solutions of D-xylose, D-ribose, D-, and L-arabinose at *ca.* 30 °C. The partial molar heat capacity at infinite dilution, $C^{\infty}_{p,2}$ was determined. Values of $C^{\infty}_{p,2}$ obtained are: D-xylose 281±2, D-ribose 271±2, D-arabinose 278±3, and L-arabinose 270±4 J K^{-1} mol^{-1}. Measurements of the heat capacity of these pentoses in the solid state, $C^{*}_{p,2}$ were carried out and the parameter $\Delta C^{\infty}_{p,2} \equiv C^{\infty}_{p,2} - C^{*}_{p,2}$ was evaluated. Values of $\Delta C^{\infty}_{p,2}$ are smaller than the corresponding values for hexose obtained previously. Similarly as had been the case for hexose, the additivity parameters of the group contribution on $C^{\infty}_{p,2}$ of solute estimated from the data on other nonelectrolytes were not acceptable for pentose. From this point the interactions working between solute of saccharide and the solvent water are considered to have characters largely different from those of other nonelectrolyte.

In the realm of the chemistry of aqueous solution of non-electrolyte, urea and saccharides, such as glucose and sucrose, have often been taken as the most basic solutes. This is because of the facts that these solutes are stable chemicals easily available at very high purity and that many physicochemical behaviors of their aqueous solutions are quasiideal, or at least vary linearly with the content of solute up to the moderate concentration. In addition to these facts, saccharide molecules have following two important features: First, they exist in cyclic structure. Secondly, they contain both many hydrophilic and hydrophobic groups and these groups having opposite nature are arranged in close proximity in each other.

Effect of hydrophobic molecule and group of a molecule on water structure, namely, hydrophobic interaction, has attracted attention of many investigators. Measurements of specific heat capacity of a solute are one of the most powerful methods to investigate the role played by hydrophobic group.[1] Furthermore, in spite of the rapid development of solution calorimetry stimulated by the commercial production of Picker's flow calorimeter,[2] data of the specific heat capacity of solutions of saccharide were rather scare. This situation pushed us to take the measurement of the specific heat capacity of aqueous solutions of saccharides, and results on hexose (D-fructose, D-galactose, D-glucose, and D-mannose), disaccharide (lactose and maltose), and trisaccharide raffinose have already been reported.[3]

In the present paper, results of the similar measurement on four kinds of pentose, D-xylose, D-ribose, D- and L-arabinose will be presented. To obtain the values of the partial molar heat capacity at infinite dilution, $C^{\infty}_{p,2}$, measurements of the specific heat capacity of the sample solutions were done at ten different concentrations of solute.

Experimental

Materials. D-Xylose and L-arabinose were supplied from Nakarai Chemical Co., Ltd. while D-arabinose and D-ribose were those of Pfanstiehl Laboratories Inc. The best quality obtainable was used. Samples were dried in an electric vacuum oven held in the temperature range 90—95 °C, (for D-ribose, in the temperature range 70—75 °C as its melting point is at 86 °C). These samples were used without further purification both for solution and solid state calorimetry. Water contents of the samples determined from the decrease of mass in drying process are as follows (expressed in wt%):

D-xylose	D-ribose	D-arabinose	L-arabinose
0.056	0.267	0.356	0.175

Solution Calorimetry. Specific heat capacities of aqueous solutions of pentose were determined using a laboratory-constructed isoperibol twin calorimeter of dry shield type. The heat reservoir of the calorimeter is an aluminium block which was kept at 30±0.1 °C. As details of this calorimeter and procedures of measurements have already been reported previously,[3,4] a brief mention may be sufficient here: i) Into one of the Dewar vessels, 100 grams of solution to be examined are introduced, while the other Dewar contains always 100 g of pure water as a reference liquid. ii) Two heaters with resistance of 45.45 and 45.42 Ω are connected in series and the e.m.f. applied to the terminals of the heaters was 20.0$_0$ V. This electric power was supplied from a stabilized source, Hewlett Packard Model 6266 B. iii) The temperature rise of the solution in Dewar vessel due to the supplied electric energy was 1—2 °C and the temperature differences between the two solutions in Dewar vessels in five minutes were detected by a pair of thermistors, amplified by laboratory-made bridge and then recorded on a strip-chart recorder. The time of five minutes was read off on the recorder chart from the instance of the sudden change of the voltage.

Calibration of the Solution Calorimeter. The calibration of this calorimeter was re-taken as an initial step of the present work. As before,[3,4] the calibration was carried out using aqueous solutions of NaCl and urea for which very accurate values of the specific heat capacity have been given.[2] Following relation was obtained between the specific heat capacity of the solution C_p and the potential difference in five minutes, ΔV.

$$C_p = A + B(\Delta V) + C(\Delta V)^2.$$

On expressing C_p and ΔV in J K^{-1} g^{-1} and V, respectively, the constants A, B, and C become:

$$A = 4.1299 \pm 0.006 \text{ J K}^{-1}\text{ g}^{-1}$$

$$B = -0.0673 \pm 0.0004 \text{ J K}^{-1}\text{ g}^{-1}\text{ V}^{-1}$$

$$C = 0.0014 \pm 0.00006 \text{ J K}^{-1}\text{ g}^{-1}\text{ V}^{-2}.$$

It may seem to be strange that the introduction of 100 g

of pure water in each of the Dewar vessels does not give rise to the result of $\Delta V=0$. The phenomenon of residual heat capacity difference of the present calorimeter may be ascribed to the inequality of the weight of the two Dewar vessels (207 and 191 g).

The concentration of sample solution was corrected for the water content of the sample.

Calorimetry of Pentose in Solid State. The determination of the specific heat capacity of the pentose in solid state was carried out in Governmental Industrial Research Institute, Osaka. An apparatus, Type SH-2000 manufactured by Tokyo Rikoh Co. Ltd. was used. Specific heat capacity data obtained are those of average values in the temperature range 28—41 °C.

Results

Solution Calorimetry. Specific heat capacities of the aqueous solutions of pentose determined in the present study are summarized in Table 1. The table contains the values of ϕ_{Cp}, apparent molar heat capacity of solute, and the values of $m\phi_{C_p}$ given by the equation

$$m\phi_{C_p} = (1000 + mM_2)C_p - 1000C_{p_1},$$

where C_{p1} is the specific heat capacity of the pure solvent, water (4.1785 J K^{-1} g^{-1}), M_2 is the molar mass, and m is the molality of the solute. Similarly as in our previous work,[3,5] values of ϕ_{C_p} at infinite dilution, $\phi^{\circ}_{C_p}=C^{\infty}_{p,2}$ were determined by the least-squares fitting of the relationship,

$$m\phi_{C_p} = bm + cm^2.$$

Evidently $C^{\infty}_{p,2}$ is equal to the coefficient b.

Specific Heat Capacities of Pentose in the Solid State. Results are given in Table 2. Values of $C^{*}_{p,2}$ of D-xylose, D-arabinose, and L-arabinose are equal while a little difference is observed between these values and that of D-ribose. If an estimation procedure of the specific heat capacity of saccharide in the solid state mentioned in a previous work[3] is adopted, the calculation leads to 184 J K^{-1} mol^{-1} for furanose form of pentose. In this calculation numbers of bond taken for the stretching and vibration are for C–C, C–O, C–H, and O–H bonds, 4, 6, 6, and 4, respectively, and the number of internal rotation is 5. The excellent agreement of this value with those in Table 2 supports the estimated value of $C^{*}_{p,2}$ of raffinose in the solid state reported in our previous work.[3]

Table 1. Heat capacities C_p and calculated values of $m\phi_{Cp}$ and apparent molar heat capacity ϕ_{Cp} of aqueous solutions of pentoses as functions of molality m

	m / mol kg^{-1}	C_p / J K^{-1} g^{-1}	$m\phi_{Cp}$ / J K^{-1}	ϕ_{Cp} / J K^{-1} mol^{-1}
D-Xylose	0.2045	4.109	56.66	277.$_1$
	0.3025	4.075	81.57	269.$_7$
	0.4027	4.048	114.2	283.$_6$
	0.5026	4.018	142.7	283.$_9$
	0.6021	3.987	168.9	280.$_5$
	0.7026	3.959	198.1	282.$_0$
	0.8015	3.929	223.3	278.$_6$
	0.9007	3.903	252.3	280.$_1$
	1.002	3.876	280.6	280.$_0$
	1.105	3.849	309.0	279.$_6$
D-Arabinose	0.1999	4.110	54.85	274.$_4$
	0.2794	4.086	78.90	282.$_4$
	0.4198	4.041	117.2	279.$_2$
	0.5190	4.013	147.2	283.$_6$
	0.6086	3.988	173.9	285.$_7$
	0.7085	3.962	204.9	289.$_2$
	0.7971	3.939	231.9	290.$_9$
	0.8860	3.909	250.5	282.$_7$
	0.9790	3.889	282.1	288.$_2$
	1.079	3.867	314.9	291.$_8$
D-Riboose	0.1901	4.116	54.97	289.$_2$
	0.2791	4.086	78.71	282.$_0$
	0.3713	4.056	103.6	279.$_0$
	0.4587	4.029	128.0	279.$_0$
	0.5480	4.008	159.3	290.$_7$
	0.6384	3.981	184.1	288.$_4$
	0.7384	3.957	217.$_2$	294.$_1$
	0.8237	3.935	243.1	295.$_1$
	0.9263	3.911	276.4	298.$_4$
	1.019	3.890	306.6	300.$_9$
L-Arabinose	0.1822	4.118	52.15	286.$_2$
	0.2693	4.089	75.82	281.$_5$
	0.3820	4.055	109.1	285.$_6$
	0.4811	4.024	136.2	283.$_1$
	0.5725	3.996	161.0	281.$_2$
	0.6682	3.966	185.4	277.$_5$
	0.7626	3.939	211.5	277.$_3$
	0.8591	3.918	244.8	284.$_9$
	0.9515	3.895	272.9	286.$_8$
	1.050	3.876	308.5	293.$_8$

Discussion

In Table 2 are summarized the final results of the present work, where h is the hydration number. Hydration number was calculated from the data of the apparent molar compressibility[6] on the assumption that hydration waters are those bounded to solute which have the same compressibility as that of ice. For the sake of comparison, results on hexose obtained in our previous work[3] are also included in Table 2. Values of $C^{\infty}_{p,2}$ and $\Delta C^{\infty}_{p,2}$ are both positive, but smaller than the corresponding values of hexose. It has been demonstrated that the value of $C^{\infty}_{p,2}$ of a nonelectrolytic solute in aqueous solution can be assigned to the contribution of each component group of the solute.[7,8] In a word, the additivity rule holds for the quantity $C^{\infty}_{p,2}$. The application of the additivity parameters to saccharides, without taking account of the cyclic form of saccharide molecules, gives for pentose 161 J K^{-1} mol^{-1}, a value much smaller than those found in the present determination. This fact is not a new finding. Similar significant differences have already been found between estimated and experimental values of $C^{\infty}_{p,2}$ for monosaccharide hexose, disaccharide and trisaccharide.[3] Therefore it can be said that saccharide is not a "standard" solute as often is considered, but a solute showing very characteristic features from the point of thermochemical behavior of its aqueous solutions. The characteristic behavior of saccharide molecules in aqueous solutions

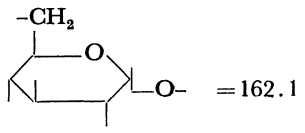
TABLE 2. VALUES OF $C^{\infty}_{p,2}$, $C^{*}_{p,2}$, $\Delta C^{\infty}_{p,2}$ (AT *ca.* 30 °C), AND HYDRATION NUMBER h (at 25 °C) OF PENTOSE AND HEXOSE IN AQUEOUS SOLUTION

	$C^{\infty}_{p,2}$ / J K^{-1} mol^{-1}	$C^{*}_{p,2}$ / J K^{-1} mol^{-1}	$\Delta C^{\infty}_{p,2}$ / J K^{-1} mol^{-1}	h / mol/mol
D-Xylose	281±2	184	97	2.6_7
D-Ribose	271±2	187	84	2.5_9
D-Arabinose	278±3	184	94	— 3.3[b]
L-Arabinose	270±4	184	86	4.0_0[c] 3.4[b]
D-Fructose	352±8	232±3	120	3.8[d]
D-Galactose	324±10	217±3	107	4.3_1
D-Glucose	331±7 322.6[a]	224±3	107	3.6_7
D-Mannose	337±5	216±3	121	3.3_1

a) Value obtained from the data found in Ref. 11. b) Value determined by the present authors. c) In Ref. 6, the distinction between D- and L-form is not mentioned. In our request, Dr. Høiland answered that they used L(+)-arabinose. d) Value found in Ref. 10.

may be interpreted as follows: The group contribution of $C^{\infty}_{p,2}$ have generally been derived for solutes which are monofunctional or α,ω-bifunctional molecules. For such solutes, effects of functional groups are isolated. However, as mentioned in the introductory part of this paper, in saccharide molecule, many functional groups are arranged in close proximity of each other on the cyclic skeleton of the molecule. As a result, effects of functional groups are overlapping and the values assigned to the contribution of each functional group on the partial molar heat capacity $C^{\infty}_{p,2}$ are not acceptable for solute of saccharide. Following values of $C^{\infty}_{p,2}$ have been observed:[3] for disaccharide lactose, 619±16 and maltose 614±20, and for trisaccharide raffinose, 931±7 J K^{-1} mol^{-1}. The $C^{\infty}_{p,2}$ varies from pentose to hexose, and from monosaccharide to di- and trisaccharide, in proportion to the molecular dimension of the saccharide molecule concerned. Therefore, the additivity rule of $C^{\infty}_{p,2}$ holds for saccharide, though the additivity parameters for saccharide should largely be different from the corresponding values obtained for other nonelectrolyte solutes. Experimental values of $C^{\infty}_{p,2}$ are much higher than those obtained by the application of the additivity rule. It follows that with regard to the contribution of group $-CH_2$, -OH, and -O- (ether), assigned respectively as 90, 9, and −57 J K^{-1} mol^{-1},[7] effects of $-CH_2$ and -OH groups seem to be strengthened, while those of -O- (ether) weakened.

Effects of solute upon the structure of solvent water are well reflected in the value of $\Delta C^{\infty}_{p,2}$, rather than that of $C^{\infty}_{p,2}$, as the intrinsic contribution of the solute in the pure state must be subtracted from the partial molar quantity, $C^{\infty}_{p,2}$. In Table 2, as the numerical values of $C^{*}_{p,2}$ are approximately constant for pentose, differences in $\Delta C^{\infty}_{p,2}$ result from differences in $C^{\infty}_{p,2}$. Values of $\Delta C^{\infty}_{p,2}$ increase with the molecular dimension of saccharide molecules, similarly as for the case of $C^{\infty}_{p,2}$. And the contribution of the structural unit of saccharide molecule to the quantity $\Delta C^{\infty}_{p,2}$ remains roughly constant in hexose, di- and trisaccharides. Here, the structural unit of saccharide is meant by



=162.1

Measurements on dextrans have shown[9] that the values of $\Delta C^{\infty}_{p,2}$ calculated for structural unit of dextran decrease with molecular weight and for dextran of M_w equal to 2.0×10^6, the value of $\Delta C^{\infty}_{p,2}$ amounts only to 3 J K^{-1} mol^{-1}.

In contrast to $C^{\infty}_{p,2}$ and $\Delta C^{\infty}_{p,2}$, hydration numbers vary randomly with solute species. Here, the term hydration corresponds to the existence of the compressed water molecules attached to solute. Hydration of saccharide is mainly ascribed to the effect of hydrophilic group -OH in the molecule. The fact that hydration number does not vary proportionally with the number of -OH group contained in saccharide molecule has been interpreted in terms of the intramolecular hydration bonding and the steric hindrance effect.[10]

The difference in the $\Delta C^{\infty}_{p,2}$ values of two stereoisomers of L- and D-arabinose is just the limit of experimental precision. This difference might be related to that the stable form of L-arabinose is pyranose form in solution, in contrast to furanose form of D-arabinose. In order to obtain further information on differences in the behavior of D- and L-arabinose, we have taken the determination of the hydration number of D- and L-arabinose at 25 °C. An ultrasonic interferometer which had long been used in our laboratory and a pycnometer were used. Results of this determination are included in Table 2, which indicate that the two stereoisomers of arabinose have the same amount of hydration. After considering these facts, it seems improper to place so much emphasis on the difference of values of $\Delta C^{\infty}_{p,2}$ of D- and L-arabinose.

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