J. Chem. Eng. Data 1990, 35, 41-43

Partial Molar Volumes and Expansibilities of Some D-Pentoses and D-Hexoses in Aqueous Solution

Špela Paljk, Cveto Klofutar,* and Milica Kač

J. Stefan Institute, E. Kardelj University of Ljubljana, 61111 Ljubljana, Yugoslavia

The densities of aqueous solutions of some monosaccharides (D-pentoses and D-hexoses) were measured up to 2.5 mol kg^{-1} in the temperature range from 293.15 to 318.15 K. The mean molar volumes of the solutions were found to be linearly dependent on the mole fraction of the solute. Thus, the partial molar volumes of solvent and solute, respectively, are concentration-independent; i.e., the partial molar volume of the solvent is equal to the molar volume of pure solvent, and the partial molar volume of the solute is equal to its value at infinite dilution. For the systems investigated, the dependence of the partial molar volumes of the solute on temperature was found to be linear. Therefore, the partial molar expansibilities of the solutes are concentration- and temperature-independent. The thermal expansion coefficients of the solute tend to decrease slightly with increasing temperature. The thermal expansion coefficients of the solutions at 298.15 K as a function of solute mole fraction were fitted to a second-degree polynomial. In addition, from the partial molecular volumes of the solutes and the respective molecular volumes of the solid solutes, it was shown that the empty volume associated with the solute molecule in aqueous solution is small and roughly the same as the empty volume associated with this molecule in the solid state.

Introduction

Monosaccharides are polyfunctional solutes that, besides hydrophilic groups (OH and -O-), also possess hydrophobic groups (CH and CH$_2$) in the solute molecule. It is known that in aqueous mixtures at equilibrium several distinct species of solute exist, i.e., the molecules have either pyranose- and/or furanose-like structures with different orientations of the OH groups (axial or equatorial) and there is a negligible fraction of species in linear form, and that the hydration is dependent on the conformational structures of the solute molecules (*1*).

We found it instructive to investigate the volumetric behavior of some monosaccharides of D-enantiomers in aqueous solutions over a wide range of concentration and temperature, with the aim of elucidating the effects of the structure of the solutes on the volumetric properties of systems, in which hydration of solutes is important.

Experimental Section

D-Pentoses (D-arabinose, D-ribose, and D-xylose, p.a., Fluka A.G.) and D-hexoses (D-galactose, p.a., Merck; D-mannose, pure, Chemapol; D-glucose, p.a., Kemika; D-fructose, pure, Merck) were dried in vacuo over P$_2$O$_5$ at room temperature for several days and used without further purification, except D-mannose, which was recrystallized from methanol.

Density Measurements. The densities of the solutions, $d_{1,2}$ (g cm^{-3}), over the concentration range from 0.1 to 2.5 mol kg^{-1} and at temperatures from 293.15 to 318.15 K in 5 K intervals were measured by means of an A. Paar digital densimeter (DMA 10). The temperature in the oscillator chamber was monitored continuously with a Hewlett-Packard Model 2804 quartz thermometer. At a definite temperature, for each solute investigated, at least eight aqueous solutions of different concentrations were used for the density measurements.

The densities of the solutions were calculated from

$$d_{1,2} = d_1^0 + \frac{1}{A}(\tau^2 - \tau_1^2) \qquad (1)$$

where d_1^0 is the density of pure water (*2*); τ and τ_1 are the periods of oscillation in the case of solution and solvent, respectively; and A is an empirical constant, determined by measuring the periods of oscillations of pure water and air, respectively, at a definite temperature (*3*).

Results and Discussion

The mean molar volume of solution, $V_{1,2}$ (cm^3 mol^{-1}), was calculated from the experimental density data, $d_{1,2}$ (g cm^{-3}), by the relation

$$V_{1,2} = \frac{mM_2 + 1000}{(n_1 + m)d_{1,2}} \qquad (2)$$

where M_2 (g mol^{-1}) is the molecular mass of the solute investigated [M_2(pentose) = 150.131 g mol^{-1}, M_2(hexose) = 180.157 g mol^{-1}], n_1 is the number of moles of solvent (n_1 = 55.5083 mol for aqueous solution), and $n_2 \equiv m$ is the number of moles of solute per kilogram of solvent.

For the systems investigated, it was observed that at a definite temperature the mean molar volume of the solution

$$V_{1,2} = \bar{V}_1 + (\bar{V}_2 - \bar{V}_1)X_2 \qquad (3)$$

depends linearly on the mole fraction of solute, X_2. Consequently, the partial molar volume of solvent, $\bar{V}_1$, and solute, $\bar{V}_2$, is concentration-independent and equal to its value at infinite dilution; i.e., $\bar{V}_1 = \bar{V}_{1,0} = V_1^0$, where V_1^0 is the molar volume of pure solvent, and $\bar{V}_2 = \bar{V}_{2,0}$. The values of $\bar{V}_{2,0}$, determined by the method of least squares via eq 3, are given in Table I, together with the available literature data at 298.15 K. In the calculations, the linear regression coefficient R was greater than 0.999 99 and the values of $\bar{V}_{1,0}$ differed by less than ±0.025% from the molar volume of pure water at a definite temperature, calculated from the respective density data of pure water. The values listed in Table I indicate that the behavior of water differs within each group of solutes, which differ only in possible conformation forms. In addition, from Table I, it can be seen that our values of $\bar{V}_{2,0}$ at 298.15 K, relative to the mean values of $\bar{V}_{2,0}$ obtained by other authors, are higher by 0.7% for D-arabinose, 0.2% for D-ribose, 1.2% for D-xylose, 0.2% for D-galactose, 0.8% for D-mannose, 0.7% for D-glucose, and 2.4% for D-fructose, respectively.

For the investigated systems, the dependence of the partial molar volume of the solute on temperature is linear. Consequently, the partial molar expansibility of the solute, $\bar{E}_2 = (\delta\bar{V}_2/\delta T)_P$, is temperature-independent and, because $\bar{V}_2 = \bar{V}_{2,0}$, is equal to its value at infinite dilution, $\bar{E}_2 = \bar{E}_{2,0}$. The values of $\bar{E}_{2,0}$, obtained by the method of least squares, are given in Table II, together with the values of $\bar{E}_{2,0}$ for D-ribose, D-glucose, and D-fructose from the literature.

The values of the thermal expansion coefficient of the solutes at infinite dilution, defined as $\alpha_{2,0} = (1/\bar{V}_{2,0})(\delta\bar{V}_{2,0}/\delta T)_P =$

0021-9568/90/1735-0041$02.50/0

Table I. Values of Partial Molar Volume of the Solutes at Infinite Dilution in the Temperature Range Studied

solute	$\bar{V}_{2,0}/(\mathrm{cm^3\ mol^{-1}})$					
	T = 293.15 K	T = 298.15 K[a]	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15 K
D-pentoses						
D-arabinose	93.8 ± 0.2	94.2 ± 0.2	94.6 ± 0.2	95.1 ± 0.2	95.5 ± 0.2	96.0 ± 0.2
D-ribose	95.0 ± 0.1	95.5 ± 0.1	95.9 ± 0.1	96.5 ± 0.2	97.0 ± 0.2	97.4 ± 0.2
D-xylose	96.1 ± 0.3	96.4 ± 0.3	96.7 ± 0.3	97.1 ± 0.3	97.3 ± 0.3	97.5 ± 0.3
D-hexoses						
D-galactose	110.8 ± 0.2	111.1 ± 0.2	111.5 ± 0.2	111.9 ± 0.3	112.2 ± 0.3	112.5 ± 0.4
D-mannose	112.3 ± 0.6	112.6 ± 0.6	113.1 ± 0.6	113.4 ± 0.6	113.8 ± 0.6	114.1 ± 0.5
D-glucose	112.4 ± 0.1	112.7 ± 0.1	113.3 ± 0.2	113.5 ± 0.1	113.9 ± 0.2	114.2 ± 0.2
D-fructose	113.1 ± 0.1	113.4 ± 0.1	113.9 ± 0.1	114.5 ± 0.1	115.1 ± 0.1	115.5 ± 0.1

[a] Literature values of $\bar{V}_{2,0}/(\mathrm{cm^3\ mol^{-1}})$ at 298.15 K: D-arabinose, 93.2 (*4*), 93.2 (*5*), 94.0 (*6*); D-ribose, 95.2 (*4*), 95.1 (*5*), 95.56 (*6*), 95.2 (*7*), 95.3 (*8*); D-xylose, 95.4 (*4*), 95.60 (*6*), 95.2 (*9*), 94.8 ± 0.4 (*10*); D-galactose, 110.2 (*4*), 110.64 (*6*), 110.7 (*8*), 111.9 ± 0.3 (*10*); D-mannose, 111.3 (*4*), 111.96 (*6*), 111.7 ± 0.5 (*10*); D-glucose, 111.7 (*4*), 111.9 (*8*), 112.2 ± 0.4 (*10*), 111.99 (*11*), 111.9 (*12*), 111.9 (*13*), 111.3 (*14*), 111.5 (*15*), 112.3 (*16*); D-fructose, 110.88 (*6*), 110.4 ± 0.4 (*10*), 110.69 (*11*).

Table II. Values of Partial Molar Expansibility of the Solutes at Infinite Dilution in the Temperature Range Studied and Values of Thermal Expansion Coefficients of the Solutes at Infinite Dilution and 298.15 K

solute	$10^2\bar{E}_{2,0}{}^a/(\mathrm{cm^3\ mol^{-1}\ K^{-1}})$	$10^4\alpha_{2,0}/\mathrm{K^{-1}}$
D-pentoses		
D-xylose	5.8 ± 0.3	6.0 ± 0.3
D-arabinose	8.8 ± 0.2	9.3 ± 0.2
D-ribose	9.8 ± 0.3	10.3 ± 0.3
D-hexoses		
D-galactose	6.9 ± 0.3	6.2 ± 0.3
D-mannose	7.1 ± 0.1	6.3 ± 0.1
D-glucose	7.4 ± 0.5	6.6 ± 0.4
D-fructose	10.1 ± 0.5	8.9 ± 0.4

[a] Literature values of $\bar{E}_{2,0}/(\mathrm{cm^3\ mol^{-1}\ K^{-1}})$: D-ribose, 0.115, calculated from the literature values of $\bar{V}_{2,0}$ at 278.15 K and 298.15 K (*8*); D-glucose, 0.091 ± 0.002 at 298.15 K (*11*) and 0.11, calculated from the literature values of $\bar{V}_{2,0}$ at 288.15, 298.15, and 308.15 K (*14*); D-fructose, 0.136 ± 0.001 at 298.15 K (*11*).

Table III. Values of Regression Coefficients of Equation 5 with the Standard Error of the Estimate, *s*, at 298.15 K

solute	10^3a_1	-10^3a_2	10^7s
D-pentoses			
D-xylose	1.829	6.687	3.9
D-arabinose	3.490	11.454	4.7
D-ribose	4.033	14.019	4.7
D-hexoses			
D-galactose	2.179	8.558	1.5
D-mannose	2.262	8.543	3.7
D-glucose	2.477	9.935	0.8
D-fructose	3.908	15.658	2.1

Table IV. Values of Partial Molecular Volume of the Solutes in Aqueous Solutions at 293.15 K and Their Molecular Volumes and Values of the Ratio of These Values against the van der Waals Volume

solute	$10^{22}\bar{v}_{2,0}$/(cm³/molecule)	$10^{22}v_2^0$/(cm³/molecule)	$\bar{v}_{2,0}/v_\infty$	v_2^0/v_∞
D-pentoses				
D-arabinose	1.558	1.573	1.28	1.29
D-ribose	1.578		1.29	
D-xylose	1.596	1.635	1.31	1.34
D-hexoses				
D-galactose	1.840	1.915[a]	1.25	1.31
D-mannose	1.865	1.944	1.27	1.33
D-glucose	1.866	1.938[b]	1.27	1.32
D-fructose	1.878	1.872	1.28	1.28

[a] 291.15 K. [b] 298.15 K.

$\bar{E}_{2,0}/\bar{V}_{2,0}$ (K) at 298.15 K are given in Table II, also. It can be seen that the values of $\bar{E}_{2,0}$ as well as of $\alpha_{2,0}$ increase in the order D-xylose < D-arabinose < D-ribose for the D-pentoses and D-galactose < D-mannose < D-glucose < D-fructose for the D-hexoses. The listed values of thermal expansion coefficients for the investigated carbohydrates are close to the $\alpha_{2,0}$ values for cyclic ethers, e.g., tetrahydrofuran, tetrahydropyran, and trimethylene oxide (*17*). On the other hand, the values of $\alpha_{2,0}$ for the investigated systems tend to decrease slightly with increasing temperature, as was observed previously for compounds having more than one OH group (*13*).

The coefficient of thermal expansion of the solutions at 298.15 K, $\alpha_{1,2} = (1/V_{1,2})(\delta V_{1,2}/\delta T)_P$, were calculated from the relation

$$\alpha_{1,2} = \frac{1}{V_{1,2}}[E_1^0 + (\bar{E}_{2,0} - E_1^0)X_2] \qquad (4)$$

where $E_1^0 = (\delta V_1^0/\delta T)_P = \alpha_1^0 V_1^0$ is the molar expansibility of the solvent and α_1^0 is the thermal expansion coefficient of pure solvent. The value of the thermal expansion coefficient of water was taken from ref 2. The concentration dependence of $\alpha_{1,2}$ against mole fraction of solute at 298.15 K was expressed analytically in the form

$$\alpha_{1,2} - \alpha_1^0 = a_1X_2 + a_2X_2^2 \qquad (5)$$

The values of the regression coefficients of eq 5, obtained by the method of least squares, are given in Table III.

The partial molar volume of a solute at infinite dilution can be assumed to be the sum of the relatively large intrinsic volume of solute and the minor contribution from the so-called empty volume. In Table IV, the values of partial molecular volume, $\bar{v}_{2,0}$ (cm³/molecule), for the investigated solutes in aqueous solutions, calculated from their partial molar volumes, $\bar{v}_{2,0} = \bar{V}_{2,0}/N$, where N is the Avogadro constant, and the values of the molecular volume of the solid solutes, v_2^0 (cm³/molecule), calculated from $v_2^0 = M_2/d_2^0N$, are given at 293.15 K, except for D-galactose at 291.15 K and D-glucose at 298.15 K. The densities of solid solutes, d_2^0 (g cm⁻³) were taken from ref 18. A comparison of the partial molecular volumes with the molecular volumes shows that the partial molecular volumes are very slightly smaller, except for D-fructose, where $\bar{v}_{2,0} \cong v_2^0$. So, the values of excess partial molecular volume, $\bar{v}_{2,0}^{\mathrm{ex}}$ (cm³/molecule) = $\bar{v}_{2,0} - v_2^0$, which characterizes the volume changes associated with the transfer of one molecule of pure monosaccharide to an infinitely diluted solution, are very small and negative, except for D-fructose. On this basis, it may be concluded that the empty volume associated with the solute molecule in aqueous solution is roughly the same as the empty volume associated with this molecule in the solid state. Thus, the values of the ratio $\bar{v}_{2,0}/v_\infty$, where v_∞ is the van der Waals molecular volume, calculated from the van der Waals increments of atoms in solute molecules (*19*), range from 1.25 for D-galactose to 1.31 for D-xylose. The value of $\bar{v}_{2,0}/v_\infty = 1.27$ for D-glucose is equal to that given in ref 19. On the other hand, the values of the ratio v_2^0/v_∞ range from 1.28 for D-fructose to 1.34 for D-xylose. From these values, it follows that the empty volume of the solutes investigated either in crystal form or in aqueous solution occupies about one fourth of their total volume. These results are close to those given previously for relatively polar molecules (*19*). For such molecules, the empty volume around them in the crystal is small due to the strong forces holding them together. Such molecules also have a small empty volume associated with them in aqueous solution because of their strong attraction to the polar water molecules, which results in a shrinkage of the empty volume.

Acknowledgment

We thank J. Burger for her skillful technical assistance.

Literature Cited

(1) Franks, F. *Pure Appl. Chem.* **1987**, *59*, 1189.
(2) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97.
(3) *Digital Densimeter for Liquids and Gases*; Anton Paar K. G.: A-8054 Graz, Austria.
(4) Høiland, H.; Holvik, H. *J. Solution Chem.* **1987**, *7*, 587.
(5) Morel, J. P.; Lhermet, C.; Morel-Desrosiers, N. *Can. J. Chem.* **1988**, *64*, 996.
(6) Jasra, R. V.; Ahluwalia, J. C. *J. Solution Chem.* **1982**, *11*, 325.
(7) Uedaira, H.; Uedaira, H. *J. Solution Chem.* **1985**, *14*, 27.
(8) Franks, F.; Ravenhill, J. R.; Reid, D. S. *J. Solution Chem.* **1972**, *1*, 3.
(9) Uedaira, H.; Uedaira, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2137.
(10) Shahidi, F.; Farrell, P. G.; Edward, J. T. *J. Solution Chem.* **1976**, *5*, 807.
(11) Bernal, P. J.; Van Hook, W. A. *J. Chem. Thermodyn.* **1988**, *18*, 955.
(12) Longsworth, L. G.; Shedlovsky, T., Ed. *Electrochemistry in Biology and Medicine*; Wiley: New York, 1955; Chapter 19.
(13) Neal, J. L.; Goring, D. A. I. *J. Phys. Chem.* **1970**, *74*, 658.
(14) Miyajima, K.; Sawada, M.; Nakagaki, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1954.
(15) Neal, J. L.; Goring, D. A. I. *Can. J. Chem.* **1970**, *48*, 3745.
(16) Kiyosawa, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 633.
(17) Cabani, S.; Conti, G.; Matteoli, E. *J. Solution Chem.* **1976**, *5*, 751.
(18) *Handbook of Chemistry and Physics*; Hodgman, C. D., Ed.; Chemical Rubber: Cleveland, OH, 1957.
(19) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 26.

Received for review January 11, 1989. Accepted September 18, 1989. We thank the Slovene Research Community for financial support.

Solubility of Carbon Dioxide in *n*-Tetracosane and in *n*-Dotriacontane

Fuan-Nan Tsai* and Jun-Shun Yau

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 70101, R.O.C.

The solubility of carbon dioxide in *n*-tetracosane and *n*-dotriacontane has been measured in a semiflow apparatus over the temperature range from 100 to 300 °C at pressures up to 50 atm. Henry's constant and the partial molar volume at infinite dilution are determined from the solubility data.

Introduction

The solubility of carbon dioxide in heavy paraffins is of interest in some industrial processes, notably Fischer–Tropsch syntheses. Robinson et al. (*1–3*) have measured the solubility of carbon dioxide in several heavy *n*-paraffins, in the cycloparaffins cyclohexane and *trans*-decalin, and in several aromatic solvents at temperatures to 160 °C. Chao et al. (*4–6*) have reported the solubility of carbon dioxide in *n*-hexatriacontane, *n*-octacosane, and *n*-eicosane over the temperature range of 100–300 °C and at pressures from 10 to 50 atm. In the present study, the solubility of carbon dioxide in *n*-tetracosane (n-C_{24}) and *n*-dotriacontane (n-C_{32}) at temperatures up to 300 °C and pressures to 50 atm has been determined. Henry's constant and the partial molar volume at infinite dilution of the dissolved gas are obtained from the data.

Experimental Section

The experimental apparatus used for the measurement of gas solubility was a semiflow vapor–liquid equilibrium apparatus. Detailed description of the equipment and sampling procedure has been reported (*7*). Briefly, a gas stream from a high-pressure cylinder is passed through two cells in series containing the hydrocarbon liquid. The first cell is the presaturator and the second the equilibrium cell. Upon saturation, the sample from the latter is withdrawn, reduced in pressure, and collected in a trap. The collected hydrocarbon is weighed with an analytical balance, and the liberated gas from the trap is measured volumetrically in a buret for the liquid phase and in a wet test meter for the gas phase. Temperature of the

Table I. Solubility Data of Carbon Dioxide in *n*-Tetracosane

T, °C	*P*, atm	*x*	*y*	*K*
100.0	10.0	0.0819	1.0000	12.22
	20.0	0.1720	1.0000	5.814
	30.0	0.2437	1.0000	4.103
	40.0	0.3004	1.0000	3.329
	50.0	0.3531	1.0000	2.832
200.0	10.0	0.0646	0.9996	15.47
	20.0	0.1228	0.9997	8.141
	30.0	0.1762	0.9998	5.674
	40.0	0.2284	0.9998	4.377
	50.0	0.2705	0.9999	3.696
300.0	10.0	0.0595	0.9889	16.62
	20.0	0.1127	0.9937	8.817
	30.0	0.1612	0.9951	6.173
	40.0	0.2060	0.9957	4.833
	50.0	0.2533	0.9961	3.932

Table II. Solubility Data of Carbon Dioxide in *n*-Dotriacontane

T, °C	*P*, atm	*x*	*y*	*K*
100.0	10.0	0.1008	1.0000	9.921
	20.0	0.1971	1.0000	5.074
	30.0	0.2701	1.0000	3.702
	40.0	0.3371	1.0000	2.966
	50.0	0.3962	1.0000	2.524
200.0	10.0	0.0714	1.0000	14.01
	20.0	0.1465	1.0000	6.826
	30.0	0.2010	1.0000	4.975
	40.0	0.2582	1.0000	3.873
	50.0	0.3074	1.0000	3.253
300.0	10.0	0.0649	0.9989	15.39
	20.0	0.1260	0.9994	7.932
	30.0	0.1868	0.9995	5.351
	40.0	0.2367	0.9995	4.223
	50.0	0.2839	0.9996	3.521