BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2137—2140 (1969)

Activity Coefficients of Aqueous Xylose and Maltose Solutions

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(Received December 16, 1968)

Osmotic and activity coefficients of aqueous xylose and maltose solutions at 25°C are measured by the isopiestic vapor pressure method. Densities of these solutions are also determined at 25°C. The activity coefficients of water in these solutions show that both xylose and maltose solutions do not behave as regular solutions. Second virial coefficients for xylose and maltose are calculated from partial molar volumes of the solute and the solvent at infinite dilution and empirical equations of water activity coefficient. The coefficients calculated for xylose and maltose are 111 and 248 cc/mol, respectively. Second virial coefficients for these sugars and a few other sugars are approximately proportional to the molecular weight. This relation is explained by the van der Waals model.

The tendency of nonpolar solute to adhere to one another in aqueous environment is affected by the addition of sugars to the system. The protective action of sugars, including xylose, glucose and sucrose, in the coagulation of plasma proteins has been found by Hardt *et al.*[1] They showed that the degree of the action varied with sugars. In a previous paper,[2] we have reported that sucrose affected the hydrophobic bonding between dye ions and decreased the self-association of dyes.

The influence of the addition of sugars on the aqueous solutions of protein and nonpolar solute can be explained by the thermodynamic properties of aqueous sugar solutions. Activity coefficient has been obtained, however, so far only for glucose,[3] sucrose[4] and raffinose.[5] Stigter[6] and Kozak *et al.*[7] calculated the second virial coefficients for these three sugars from the activity and density data.

In the present work, osmotic and activity coefficients of maltose and xylose solutions were determined by the isopiestic vapor pressure method. Density was measured for these two systems. The second virial coefficients of these sugars were calculated by the method of Kozak *et al.*[8]

Experimental

Materials. Maltose (G. R.) and xylose (G. R.) were purified by crystallization repeated two or three times from water-ethanol solutions. Potassium chloride of analytical grade (Merck Co.) was used without further purification. These samples were dried *in vacuo* over phosphorus pentoxide at 100°C. Solutions were made up in conductance water which was air-freed by boiling before use.

Isopiestic Vapor Pressure Method. Osmotic and activity coefficients were determined with an apparatus similar to that employed by Robinson and Stokes.[4] About 2 m*l* of the sample solution was placed in each of two or three cylindrical silver dishes with lids. The reference potassium chloride solution was also placed in another set of silver dishes. These dishes were placed on a flat copper block contained in a vacuum desiccator, which was set in a thermostat bath at 25°C, controlled to ±0.01°C. At the start of the run, the hinged lids of the dishes were held open by a similar device as described by Robinson and Stokes.[4] The desiccator was evacuated to about 20 mmHg. In order to stir the solution the desiccator was rocked once every four or five seconds. Stirring was made by 3 mm pyrex glass spheres rolling across the bottom of the dishes. At the end of the run, after each dish was closed the vacuum was broken. Equilibrium concentration was measured by weighing the dishes. All the weights were corrected to vacuum. The time required for the equilibrium to be attained was 48 to 90 hr.

Calculation of the Osmotic and the Activity Coefficients. The osmotic coefficient of sugar, ϕ, is given by

$$\phi = 2m_R\phi_R/m\,, \tag{1}$$

where m_R and m are the molal concentrations of reference solute potassium chloride and sugar in isopiestic equilibrium, respectively. ϕ_R is the osmotic coefficient of potassium chloride at the concentration m_R. The values of the osmotic coefficient for potassium chloride solutions were tabulated by Robinson and Stokes.[8] The osmotic coefficients for each system were represented by the equations of the form

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[1] C. R. Hardt, I. F. Muddleson and C. D. Ball, *J. Biol. Chem.*, **163**, 211 (1946).

[2] H. Uedaira and H. Uedaira, *Kolloid Z. Z. für Polym.*, **194**, 148 (1964).

[3] J. B. Taylor and J. S. Rowlinson, *Trans. Faraday Soc.*, **51**, 73 (1955).

[4] R. A. Robinson and R. H. Stokes, *J. Am. Chem. Soc.*, **65**, 1954 (1961).

[5] H. D. Ellerton, G. Reinfelds, D. E. Mulcahy and P. J. Dunlop, *J. Phys. Chem.*, **68**, 398 (1964).

[6] D. Stigter, *ibid.*, **64**, 118 (1960).

[7] J. J. Kozak, W. S. Knight and W. Kauzmann, *J. Chem. Phys.*, **48**, 675 (1968).

[8] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth Scientific Publications, London (1959).

$$\phi = 1 + am + bm^2 + cm^3 . \qquad (2)$$

The coefficients a, b and c were obtained by the method of least squares.

From the Gibbs-Duhem relation and the definition of ϕ, the activity coefficient of solute, γ, is shown by

$$\ln \gamma = (\phi - 1) + \int_0^m (\phi - 1) \mathrm{d} \ln m$$
$$= 2am + \frac{3}{2} bm^2 + \frac{4}{3} cm^3. \qquad (3)$$

The activity coefficient of solvent water, γ_w, was expressed as a power series in the mole fraction of the solute, x. For solutions of nonelectrolytes we have

$$\ln \gamma_w = Bx^2 + Cx^3 + Dx^4 . \qquad (4)$$

The coefficients B, C and D have the form7),[*1]

$$B = -\left[\frac{1}{2} + a\frac{10^3}{W}\right], \qquad (5)$$

$$C = -\left[\frac{2}{3} + 2a\frac{10^3}{W} + b\left(\frac{10^3}{W}\right)^2\right], \qquad (6)$$

$$D = -\left[\frac{3}{4} + 3a\frac{10^3}{W} + 2b\left(\frac{10^3}{W}\right)^2 + c\left(\frac{10^3}{W}\right)^3\right], \qquad (7)$$

where W is the molecular weight of water.

Density Measurements and the Calculation of Partial Molar Volumes. Density measurements were performed at 25±0.01°C with springel pycnometers of 30 ml capacity. At higher concentration of maltose solutions, that of 10 ml capacity was used. The density values for each system were fitted to the equations of the form

$$d = d_o + A_1 m + A_2 m^2 + A_3 m^3 . \qquad (8)$$

From Eq. (8), specific volume V is obtained.

$$V = \frac{1}{d_o} - \frac{A_1}{d_o} m + \left(\frac{A_1^2}{d_o^3} - \frac{A_2}{d_o^2}\right) m^2$$
$$+ \left(-\frac{A_1^3}{d_o^4} + \frac{2A_1A_2}{d_o^3} - \frac{A_3}{d_o^2}\right) m^3$$
$$+ \left(\frac{A_1^4}{d_o^5} - \frac{3A_1^2A_2}{d_o^4} + \frac{A_2^2 + 2A_1A_3}{d_o^3}\right) m^4 + \cdots . \qquad (9)$$

Partial molar volumes of water, $\bar{v}_1$, and of solute, $\bar{v}_2$, can be calculated by the equations

$$\bar{v}_1 = W \cdot V - [(1000 + mM) mW/1000](\partial V/\partial m) , \qquad (10)$$

$$\bar{v}_2 = M \cdot V + (1000 + mM)(\partial V/\partial m) , \qquad (11)$$

where M is the molecular weight of the solute.

Results

The experimental values of the equilibrium molalities of xylose and maltose, and the molalities of the corresponding potassium chloride solutions are given in Table 1. The osmotic coefficients calculated by Eq. (1) are also given. These coefficients of xylose and maltose solutions are represented by the following equations.[*2]

$$\phi_{\mathrm{xy}} = 1 + 0.01407m + 0.002288m^2 - 0.000482m^3 \qquad (12)$$

$$\phi_{\mathrm{mal}} = 1 + 0.03635m + 0.001818m^2 - 0.002405m^3 \qquad (13)$$

The slope of the osmotic coefficient-concentration curves increases in the order

xylose < glucose < maltose < sucrose < raffinose.

From Eqs. (3), (4), (12) and (13), the expressions of activity coefficients of the solute and the solvent were obtained. They are for xylose solution,

$$\ln \gamma_{\mathrm{xy}} = 0.02814m + 0.003432m^2 - 0.0006427m^3 , \qquad (14)$$

$$\ln \gamma_{\mathrm{w,xy}} = -1.281x^2 - 9.093x^3 + 65.61x^4 , \qquad (15)$$

and for maltose solution

$$\ln \gamma_{\mathrm{mal}} = 0.007270m + 0.02727m^2 - 0.003207m^3 , \qquad (16)$$

$$\ln \gamma_{\mathrm{w,mal}} = -2.518x^2 - 60.71x^3 + 302.5x^4 . \qquad (17)$$

In contrast to glucose solutions,3) none of xylose, maltose and sucrose4) solutions behave as regular solutions.

TABLE 1. ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND XYLOSE OR MALTOSE AT 25°C

m_{R}	m_{xy}	ϕ_{xy}	m_{R}	m_{mal}	ϕ_{mal}
0.30924	0.55618	1.007_2	0.33268	0.58406	1.030_4
0.47150	0.83631	1.014_3	0.41508	0.72443	1.032_6
0.55423	0.97815	1.017_7	0.42119	0.73320	1.035_1
0.72969	1.2850	1.018_7	0.51480	0.88687	1.043_2
0.90713	1.5831	1.028_1	0.56039	0.96097	1.047_3
1.1436	1.9874	1.033_7	0.72969	1.2273	1.066_6
1.3158	2.2876	1.035_2	0.98979	1.6203	1.096_4
1.6413	2.8414	1.045_5	1.0114	1.6459	1.103_0
2.0112	3.4673	1.058_7	1.1436	1.8446	1.113_4
			1.3155	2.0844	1.135_9
			1.6379	2.5369	1.168_5
			2.0112	3.0356	1.209_2

[*1] Two misprints are found in Kozak's equations (11) and (12). In the coefficient of the term of x^3, $b(10^3/W)$ should be $b(10^3/W)^2$, and in the coefficient of term of x^4, $3b(10^3/W)^2$ should be $2b(10^3/W)^2$.

[*2] An IBM 7090 computer was used for all the calculations by the method of least squares.

TABLE 2. DENSITY OF AQUEOUS XYLOSE AND MALTOSE SOLUTIONS AT 25°C

m	d (g/ml)
Xylose	
0.026610	0.99854
0.039512	0.99922
0.053683	0.99997
0.067322	1.0007
0.13553	1.0044
0.27789	1.0120
0.50056	1.0232
0.99509	1.0465
1.5812	1.0715
2.2569	1.0971
2.9975	1.1221
Maltose	
0.30617	1.0352
0.59583	1.0670
0.99162	1.1049
1.4480	1.1421
2.3365	1.1996
2.8692	1.2275

Densities of xylose and maltose solutions are shown in Table 2, and are represented by the equations

$$d_{xy} = 0.99707 + 0.05505m - 0.00572m^2 + 0.000426m^3, \qquad (18)$$

$$d_{mal} = 0.99707 + 0.13122m - 0.02505m^2 + 0.002551m^3. \qquad (19)$$

From Eqs. (8), (9), (10), (11), (18) and (19), partial molar volumes of water and xylose in aqueous xylose solution are

$$\bar{v}_1 = 18.069 + 0.009003m^2 - 0.003251m^3 + 0.002313m^4, \qquad (20)$$

$$\bar{v}_2 = 95.20 + 0.9994m + 0.2707m^2 - 0.1712m^3 + 0.01356m^4. \qquad (21)$$

and those of water and maltose in maltose solution are

$$\bar{v}_1 = 18.069 + 0.9551m^2 + 0.03240m^3 - 0.01557m^4, \qquad (22)$$

$$\bar{v}_2 = 211.3 - 106.0m + 8.025m^2 + 1.167m^3 - 0.8652m^4. \qquad (23)$$

Discussion

Activity coefficients of xylose and maltose in aqueous solutions show deviations from ideality. The behavior of these aqueous solutions can be discussed more definitely by the second virial coefficient in the osmotic virial equations.

Recently Kozak *et al.*⁷⁾ proposed the method of calculation of the second virial coefficient from water activity coefficient and partial molar volume. If compressibility effects can be neglected, and concentrarions in the osmotic virial equation expressed in molecules per unit volume, then the second virial coefficient B_2^* can be calculated by

$$B_2^* = (v_2^* - v_1^0) + v_1^0\left(\frac{1}{2} - B\right)\Big)/\boldsymbol{N}_A, \qquad (24)$$

where $\boldsymbol{N}_A$ is the Avogadoro number, v_1^0 and v_2^* the partial molar volumes of solvent and solute at infinite dilution, and B the coefficient in Eq. (4). The values of v_1^0 and v_2^* are unchanged whether $\bar{v}_1$ and $\bar{v}_2$ are expressed as a power series in the molal concentration or molar concentration, so B_2^* be calculated from Eqs. (15), (17), (20), (21), (22), and (23). The values are

$B_2^* \cdot \boldsymbol{N}_A = 111$ cc/mol for xylose in water,
$B_2^* \cdot \boldsymbol{N}_A = 248$ cc/mol for maltose in water.

The values of B_2^* for glucose and sucrose were calculated by Stigter,⁶⁾ and that for raffinose by Kozak *et al.*⁷⁾

If we take the sugars as rigid spheres with attractive tails, the second virial coefficient $B_2^*(T)$ for such a van der Waals model is⁹⁾

$$B_2^* = \left(4 - \frac{3}{64}\frac{\boldsymbol{h}\nu_0}{\boldsymbol{k}T}\frac{\alpha^2}{a^6}\right)\frac{4}{3}\pi a^3, \qquad (25)$$

where a is the radius of a molecule, α the polarizability, other symbols have their usual meanings. As α and a^3 are proportional to the molecular weight, the quantity in the parenthesis of Eq. (25) is approximately independent of the molecular weight. Therefore, B_2^* will be proportional to

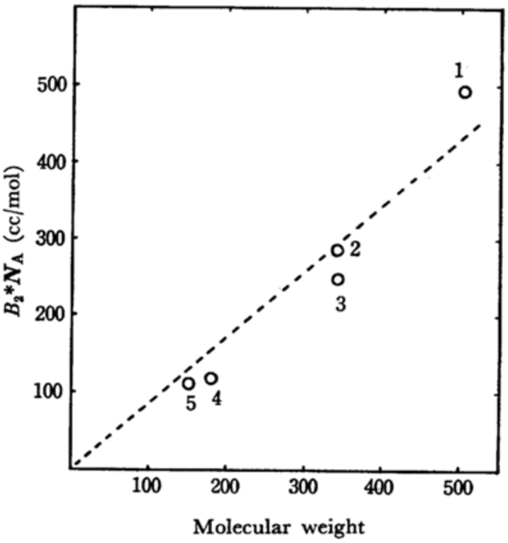

Fig. 1. The relation between second virial coefficient and molecular weight.
1: raffinose 2: sucrose 3: maltose 4: glucose 5: xylose

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9) B. Chu, "Molecular Forces," Chap. 3, John Wiley & Sons, New York, London (1967).

the molecular weight. In Fig. 1, the plots of the second virial coefficients *versus* molecular weights are shown. The figure shows that the relation (25) holds approximately. While maltose and sucrose have the same molecular weight, B_2^* of maltose is smaller than that of sucrose. This may be caused by the larger attractive force between maltose molecules.