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Diffusion Coefficients of Xylose and Maltose in Aqueous Solution

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Diffusion coefficients for the systems aqueous xylose solution and aqueous malotse solution at 25°C were measured by the Rayleigh interference method. Viscosities of these systems were also determined. The concentration dependence of diffusion coefficient for maltose solution is well described by the Gordon relation. For xylose solution, however, a small deviation from this relation is observed. The translational frictional coefficient of maltose was calculated by the shell model of Bloomfield *et al.* If the effect of the local viscosity around a molecule of the solute is corrected, the agreement between the calculated and the observed values is satifsactory.

Only a small amount of data on diffusion of sugars in aqueous solution can be found in literature. Studies on such sugars are limited to the application of the Stockes-Einstein relation and the Gordon empirical relation. For example, the limiting diffusion coefficient of sucrose in aqueous solution is compared with the value calculated by the Stokes-Einstein relation,[1] though the molecule of sucrose has a non-spherical shape.

We present here the viscosity data and the diffusion coefficients for xylose and maltose in the aqueous solution at 25°C. Activity coefficients and densities for these systems have been presented previously.[2] The Gordon relation is tested by these data, and the translational frictional coefficient of maltose in the solution is calculated by the shell model of Bloomfield *et al.*,[3] a comparison being made between the observed and the calculated frictional coefficient.

Experimental

Materials. Xylose and maltose were purified as before.[2]

Viscosity Measurements. An Ubbelohde viscometer was used, the flow time for water at 25°C being 373.6 sec. The correction of the kinetic energy was not made. Viscosity measurement was made at 25.00±0.01°C.

Diffusion Measurements. The diffusion experiment was performed at 25.00±0.01°C using a Spinco Model H diffusion apparatus with a Rayleigh interferometer. For typical run, eight or nine photographic exposures were made at intervals ranging from 15 min to 4 hr; 4 inch by 5 inch Kodack type M glass photographic plates were used. The concentration difference of the solution on both sides of the diffusion boundary was adjusted so that the total number of Rayleigh fringes became 50 or 60. The plates were measured with a Shimadzu type SR-2 comparator. The zero time correction was the order of several seconds. The computation of diffusion coefficients was made by the method suggested by Creeth.[4]

Deionized water was employed as the solvent for these systems. All solutions were prepared by weight, and the weighing was corrected to vaccum. The molar concentrations of solutions were calculated from the density.

Results and Discussion

Reciprocals of relative viscosities of xylose and maltose solutions are represented by the following experimental equations.

$$\eta_0/\eta = 1 - 0.337c \ (c<0.5) \tag{1}$$

for xylose solution, and

$$\eta_0/\eta = 1 - 0.851c \ (c<0.3) \tag{2}$$

for maltose solution, where c is the molarity of solute.

In Table 1, the mean concentration of each diffusion experiment and the corresponding observed

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[1] J. K. Gladden and M. Dole, *J. Am. Chem. Soc.*, **75**, 3700 (1953).

[2] H. Uedaira and H. Uedaira, This Bulletin, **42**, 2137 (1969).

[3] V. Bloomfield, W. O. Dalton and K. E. Van Holde, *Biopolymers*, **5**, 135 (1967).

[4] J. M. Creeth, *J. Am. Chem. Soc.*, **77**, 6428 (1955).

TABLE 1. AN EXPERIMENTAL TEST OF GORDON'S RELATION FOR XYLOSE SOLUTION AT 25°C

$D_0 = 7.495 \times 10^{-6}$ cm²/sec

c (mol/l)	$D_{\rm exp} \times 10^6$ (cm²/sec)	$1+c\dfrac{{\rm d}\ln y}{{\rm d}c}$	η_0/η	$D_{\rm calc} \times 10^6$ (cm²/sec)	$D_{\rm exp}/D_{\rm calc}$
0.095730	7.385	1.0121	0.968	7.341	1.006
0.18612	7.309	1.0238	0.937	7.191	1.016
0.19637	7.299	1.0252	0.934	7.177	1.017
0.27356	7.221	1.0356	0.908	7.048	1.025
0.44546	7.046	1.0598	0.850	6.752	1.044

TABLE 2. AN EXPERIMENTAL TEST OF GORDON'S RELATION FOR MALTOSE SOLUTION AT 25°C

$D_0 = 5.201 \times 10^{-6}$ cm²/sec

c (mol/l)	$D_{\rm exp} \times 10^6$ (cm²/sec)	$1+c\dfrac{{\rm d}\ln y}{{\rm d}c}$	η_0/η	$D_{\rm calc} \times 10^6$ (cm²/sec)	$D_{\rm exp}/D_{\rm calc}$
0.006305	5.179	1.0018	0.994	5.180	1.000
0.044895	5.072	1.0130	0.962	5.064	1.001
0.097604	4.910	1.0290	0.917	4.907	1.001
0.12398	4.825	1.0373	0.894	4.822	1.001
0.15109	4.755	1.0459	0.871	4.738	1.004
0.17387	4.662	1.0534	0.852	4.667	0.999
0.22598	4.496	1.0710	0.807	4.495	1.000
0.25272	4.408	1.0804	0.784	4.405	1.001

value of diffusion coefficient for the xylose solutions are given in the first two columns. The corresponding data for maltose solution are given in Table 2. Diffusion coefficients for the two systems decrease linearly with the increase of concentrations. Extrapolated diffusion coefficients are also given in these Tables. The concentration dependence of the diffusion coefficients is larger for maltose than for xylose solution.

Gosting and Morris⁵⁾ demonstrated that the observed diffusion coefficients of sucrose in dilute aqueous solutions agreed with diffusion coefficients calculated from the Gordon relation⁶⁾

$$D = D_0\left(1 + c\frac{{\rm d}\ln y}{{\rm d}c}\right)\frac{\eta_0}{\eta}, \tag{3}$$

where y was the molar activity coefficient of solute, η_0 and η the viscosities of water and the solution, and D_0 the limiting value of D as $c \rightarrow 0$.

In a previous paper,²⁾ we obtained the activity coefficients of xylose and maltose in aqueous solution at 25°C. Using the available density data,²⁾ we obtain the following experimental equations of the molar activity coefficients y

$$\ln y = 0.1237c + 0.01195c^2 \quad (c<3.0) \tag{4}$$

for xylose solution, and

$$\ln y = 0.2856c + 0.05475c^2 + 0.02720c^3 \quad (c<2.0) \tag{5}$$

for maltose solution.

It is of interest whether Eq. (3) may describe the dependence which we have observed in the diffusion coefficients upon the concentration for xylose and maltose solutions. In Table 1 for the xylose solution, the third column contains the values of $[1+c({\rm d}\ln y/{\rm d}c)]$ computed by Eq. (4). The values of η_0/η, column 4, were calculated from Eq. (1). Substitution of these values of D_0, $[1+c({\rm d}\ln y/{\rm d}c)]$ and η_0/η into Eq. (3) then gives the values of $D_{\rm calc}$, column 5. The ratio $D_{\rm exp}/D_{\rm calc}$ is given in the last column in Table 1. The arrangement of Table 2 for the maltose solution is similar to that of Table 1.

As seen from Table 2, Eq. (3) holds for the maltose solution. For the xylose solution, however, the value of $D_{\rm exp}$ is larger than that of $D_{\rm calc}$ (Table 1), and its deviation, though small, increases with the increase of concentration. It is thought that the effect of the kinetic correction term of Eq. (3) is overestimated.

Longsworth⁷⁾ suggested that the value of D_0 of different solution could be expressed by the Stokes-Einstein relation in the form

$$D_0 = \frac{\boldsymbol{k}T}{6\pi\eta_0}\left(\frac{4\pi\boldsymbol{N}_{\rm A}}{3V}\right)^{1/3} \tag{6}$$

where V is the apparent molar volume of solute, $\boldsymbol{N}_{\rm A}$ the Avogadro number, and the other symbols have their usual meanings. The apparent molar volumes at the infinite dilution for the xylose and the maltose in the solutions are 95.2 and 211.3

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5) L. J. Gosting and M. Morris, *ibid.*, **71**, 1998 (1949).

6) A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

7) L. G. Longsworth, *J. Am. Chem. Soc.*, **74**, 4155 (1952).

cc/mol, respectively.[2] Using Eq. (6) to calculate the diffusion coefficients of xylose and maltose at infinite dilution we obtained 7.311 and 5.607×10^{-6} cm²/sec, respectively, whereas the values extrapolated from the observed data are 7.495 and 5.201 $10^{-6} \times$ cm²/sec (Tables 1 and 2). The differences between the calculated and the observed values amount to 2.5 and 7.8%. Gladden and Dole[1] found that the differences between the calculated and the observed diffusion coefficients of glucose and sucrose amounted to 2.3 and 7.8%. The differences between the calculated and the observed values for xylose and glucose are small in comparison with the differences between the corresponding values for maltose and sucrose, because the molecules of xylose and glucose are nearly spherical. From this result, even for a small molecule such as maltose and sucrose, the deviation from the spherical shape has a large effect on the application of Eq. (6).

The assumption of the solvent as a continuum in the derivation of the Stokes relation implies that the dimensions of the diffusing particles are large in comparison with those of the solvent molecules. This assumption does not hold in the case of the small molecule, and its frictional coefficient is affected by the structure of solvent. In the aqueous solution, the water structure in the immediate vicinity of the solute is different from that of bulk water. Therefore, the value of η_0 of Eq. (6) must be different from that of bulk water. The translational frictional coefficient for a small molecule with any structure is not given yet. Therefore, when the equation of the frictional coefficient for a large particle is applied to the small molecule, the effect of the local viscosity must be suitably corrected.

Recently, Bloomfield, Dalton and Van Holde,[3] using the shell model, proposed the following expression for the translational frictional coefficient of the macromolecule with a structure which can be visualized as composed of n spherical subunits.

$$f = \frac{6\pi\eta_0\left(\sum_{l=1}^{n} r_l^2\right)^2}{\sum_{l=1}^{n} r_l^3 + \sum_{l=1}^{n}\sum_{s=1}^{n}{}' r_l^2 r_s^2 \langle R_{ls}^{-1}\rangle} \tag{7}$$

where R_{ls} is the distance between centers of two spherical shells of radius r_l and r_s

As the molecule of maltose consists of two identical spherical shells (glucose), the translational frictional coefficient f_M of maltose can be calculated by Eq. (7). Thus we have the expression

$$f_M = 1.3(6\pi\eta_0 r_G), \tag{8}$$

where r_G is the radius of glucose. Water structure around the glucose and the maltose in the aqueous solution is regarded as identical. Therefore, the ratio of the frictional coefficient of maltose and glucose is independent of the water structure around the solute. The frictional coefficient f_G of glucose is equal to $6\pi\eta_0 r_G$, and so $f_M/f_G = 1.3$. On the other hand, the diffusion coefficient is in inverse proportion to the frictional coefficient. The limiting diffusion coefficient of glucose in the aqueous solution at 25°C obtained by Gladden and Dole[1] is 6.75×10^{-6} cm²/sec. Thus the ratio of experimental frictional coefficient of maltose to that of glucose is

$$\frac{f_M}{f_G} = \frac{D_{0G}}{D_{0M}} = \frac{6.75 \times 10^{-6}}{5.201 \times 10^{-6}} = 1.29_7.$$

Agreement between the calculated and the observed ratio is very good, and is not accidental. Recently, we obtained a good agreement between the calculated and the observed ratio for the β-cyclodextrin in aqueous solution.[8] Generally, the frictional coefficient of the small molecule with complex shape is calculated by expression (7), if the effect of the local viscosity around the solute is corrected.

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8) H. Uedaira, H. Uedaira and K. Tsuda, presented at the Autumn Meeting of the Chemical Society of Japan, October, 1968.