

Calorimetric and Compressibility Study of Aqueous Solutions of Dextran with Special Reference to Hydration and Structural Change of Water

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ABSTRACT: Interactions between water and dextran have been investigated by measuring specific heat capacity, adiabatic compressibility, and viscosity, with dextran samples of molecular weight above 10^4 . For these measurements, a laboratory-constructed isoperibol twin calorimeter and an ultrasonic interferometer were used. The compressibility data show the existence of the water hydrated to dextran molecules, and the amount of hydration water was determined. The partial molar heat capacity was calculated for the structural unit of the dextran molecule. In the plot of $\log [\eta]$ against $\log M_w$, a downward deviation from the linear relation was observed, and this was interpreted as due to branching of the dextran molecule. The amount of hydration water and the partial molar heat capacity decreased with the increasing molecular weight of dextran. The quantity $\Delta \bar{C}_{p_2}^\circ = \bar{C}_{p_2}^\circ - C_{p_2}$ (pure state) indicates that the structural change of water caused by the dissolution of one structural unit of the dextran molecule is smaller than in the case of glucose and that the degree of the structural change of water decreases sharply with the increasing molecular weight of polymers. These results are interpreted in terms of the combination of branching and increased entanglement of the polymer chain.

KEY WORDS Partial Molar Heat Capacity / Compressibility / Dextran /
Partial Specific Compression / Hydration / Aqueous Solution / Structure of
Water /

Dextran is an anhydroglucose polymer mainly consisting of α -1,6-glucosidic linkages, and dissolves readily in water. Its solution properties have called not only the attention of polymer scientists but also that of biochemists. To obtain information about the interactions of dissolved dextran molecules in aqueous solution, many techniques have been applied, such as measurements of adiabatic compressibility,^{1,2} viscosity,²⁻⁴ light scattering,³ sedimentation velocity,^{3,4} and ultrasonic absorption coefficients.⁵ Earlier studies^{3,4} have been discussed by Gekko and Noguchi² in connection with their study of oligodextran. Most workers have been interested in the conformation of the dissolved dextran molecules, but the discussion on the structural change of solvent water have often been ignored. In view of this situation, we have undertaken a determination of adiabatic compressibility,

viscosity, and partial specific volume of dextran in addition to that of the partial molar heat capacity of the aqueous solutions of dextran. The partial molar heat capacity of a solute is that quantity which reflects the structural change in the solvent. Dextran samples of molecular weight above 10^4 were used.

EXPERIMENTAL

Dextran

The specimens used were supplied by Pharmacia Fine Chemical (Sweden). Table I is a reproduction of the data sheet supplied. In response to our request, the comment was given from the agency, Pharmacia Japan Co. that these specimens were produced by the B-512 strain of *Leuconostoc mensesteroides* and were purified by the fractional precipitation using ethanol. This strain is the same

Table I. Molecular weights of the dextrans used and the values of $[\eta]$ in water given in the supplied data sheet

	T 10	T 40	T 110	T 500	T 2000
$M_w/10^4$	0.94	4.0	11	50	200
$M_n/10^4$	0.55	3.0	7.6	35 ^a	143 ^a
$[\eta]$ (20°C)	0.096	0.21	0.32	—	0.70

^a Estimated by us from the ratio of M_w/M_n for T 110.

as that used by Senti *et al.*³ and Granath.⁴ Dextran is hygroscopic so that before use, the samples were dehydrated in a vacuum electric oven at 90–95°C.

The water content of the original samples was in the range of about 5–10 wt%.

Apparatus and Procedures

The adiabatic compressibility of aqueous solutions of dextran was determined by measuring the ultrasonic velocity and density. An improved ultrasonic interferometer working at 4 MHz was used. The density was determined by an Ostwald-type pycnometer of 20 cm³ capacity. The specific heat capacity of the solution was measured using an isoperibol twin calorimeter. The details of this calorimeter and the experimental procedures of the solution calorimetry are described elsewhere.^{6,7} Viscosity was measured using an Ubbelohde-type viscometer and the intrinsic viscosity $[\eta]$ was determined by the usual method. Determination of the specific heat capacity of the solution was carried out at about 30°C, while other properties were measured at 25°C.

RESULTS AND DISCUSSION

Results of viscosity measurements on aqueous solutions of dextran are shown in Figure 1, where $\log [\eta]$ is plotted against $\log M_w$. Our results agree satisfactorily with those of Senti *et al.*³ who obtained the relation $[\eta] = 9.78 \times 10^{-4} M_w^{0.50}$ for fractions of dextran with molecular weights below about 10^5 (the dotted line in Figure 1). Senti *et al.* argued that a downward deviation from the linear relation is attributable to the branching of dextran molecules. It has been observed that more highly branched dextran molecules have smaller intrinsic viscosities.⁴ If the number-average molecular weight M_n is used in place of M_w , Senti's relation reduces to

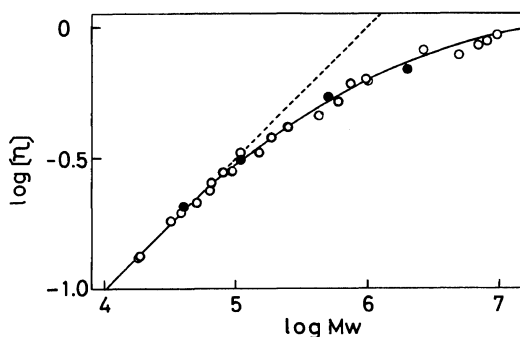


Figure 1. Double-logarithmic plot of intrinsic viscosity, $[\eta]$, against M_w for dextran in water at 25°C: ●, present work; ○, Senti *et al.*³

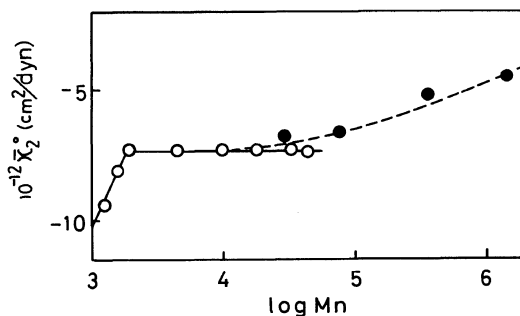


Figure 2. Molecular weight dependence of partial specific compressibility of dextran in water at 25°C: ●, present work; ○, Gekko and Noguchi.²

$[\eta] = 1.09 \times 10^{-3} M_n^{0.5}$, while Gekko and Noguchi,² using dextran samples supplied by the Central Research Institute of Meito Sangyo Co. have obtained the relation $[\eta] = 4.93 \times 10^{-4} M_n^{0.60}$ for oligodextran of M_n between 2000 and 4.5×10^4 . The differences observed between these two measurements^{2,4} are significant. Therefore, it seems that the characteristics of two kinds of dextrans are different to some extent. In what follows, a comparison will be presented between the results of Gekko and Noguchi² and ours but a part of the observed differences arises from the differences in the specimens used.

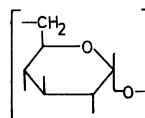
The limiting partial specific adiabatic compressibility of a solute, $\bar{\kappa}_2^\circ$, was obtained by extrapolating the data for the compressibility and density of the solution to infinite dilution.⁸ $\bar{\kappa}_2^\circ$ is defined by

$$\bar{\kappa}_2^\circ = -\frac{\kappa_1}{\bar{v}_2^\circ} \left(\frac{\partial \bar{v}_2}{\partial p} \right)^\circ$$

where \bar{v}_2° is the partial specific volume of the solute, p is the pressure and the superscript zero refers to infinite dilution. The variation of $\bar{\kappa}_2^\circ$ with M_n is illustrated in Figure 2, together with the results given by Gekko and Noguchi.² In correspondence with the results from viscosity measurements, for M_n above 5×10^4 , the values of $\bar{\kappa}_2^\circ$ deviate from a constant value of $-7.3 \times 10^{-12} \text{ cm}^2 \text{ dyn}^{-1}$ obtained for M_n between 2×10^3 and 5×10^4 , and increase with M_n . Since a value of about $20 \times 10^{-12} \text{ cm}^2 \text{ dyn}^{-1}$ is almost the lower limit for "normal" polymers such as polystyrene and poly(vinyl acetate) in very poor solvents, the negative values for dextran in water indicate a marked compacting of the polymer by the immobilization of the neighbouring water molecules (hydration). The amount of hydration water can be estimated by assuming that the solute is incompressible and that the compressibility of hydration water is identical with that of ice, $18 \times 10^{-12} \text{ cm}^2 \text{ dyn}^{-1}$.⁹ The amount of hydration water, ω , is proportional to $\bar{\kappa}_2^\circ$, ($\omega = -\bar{v}_2^\circ \bar{\kappa}_2^\circ / (\kappa_1 - \kappa_{ice})$), so that the dependence of

the amount of hydration on the molecular weight of dextran is the same as that of $\bar{\kappa}_2^\circ$. Hydration decreases with increasing molecular weight of dextran. The amount of hydration water thus determined is given in the fourth column of Table III.

Experimental results of solution calorimetry of dextran are given in Table II. In this table, the structural unit of dextran



= 162.1 was taken to calculate molecular weights, with the end effect and branching of the polymer chain being neglected. The partial molar heat capacity of the aqueous solution of dextran at infinite dilution, C_{p2}° , was calculated by use of the expression, $m\phi_{C_p} = bm + cm^2$, where ϕ_{C_p} is the apparent molar heat capacity.

The quantity $m\phi_{C_p}$ was expressed in terms of the

Table II. Specific heat capacities of aqueous solutions of dextrans at *ca.* 303 K

(a) Dextran T 10			(c) Dextran T 110		
m	C_p	$m\phi_{C_p}$	m	C_p	$m\phi_{C_p}$
mol kg ⁻¹	J g ⁻¹ K ⁻¹	J K ⁻¹	mol kg ⁻¹	J g ⁻¹ K ⁻¹	J K ⁻¹
0.4472	4.009	121	0.1171	4.128	27.7
0.5743	3.968	159	0.2161	4.086	50.3
0.6834	3.938	196	0.3284	4.046	83.1
0.7701	3.914	224	0.4317	4.008	110
0.8939	3.879	262	0.5406	3.967	136
1.0189	3.838	294	0.6661	3.931	177
1.1423	3.805	332	0.7668	3.879	183

(b) Dextran T 40			(d) Dextran T 2000		
m	C_p	$m\phi_{C_p}$	m	C_p	$m\phi_{C_p}$
mol kg ⁻¹	J g ⁻¹ K ⁻¹	J K ⁻¹	mol kg ⁻¹	J g ⁻¹ K ⁻¹	J K ⁻¹
0.3367	4.050	92.3	0.1124	4.132	29.0
0.4509	4.009	123	0.2348	4.079	55.6
0.5610	3.967	150	0.3430	4.027	72.0
0.6810	3.926	181	0.4788	3.970	99.4
0.7913	3.890	210	0.5756	3.947	137
0.9000	3.852	236	0.6880	3.906	163
1.0003	3.821	262	0.8383	3.786	122

Table III. Physical parameters of dextrans in water

Specimen	$[\eta]$	\bar{v}_2°	ω	$\bar{\kappa}_2^\circ$	$\bar{C}_{p_2}^\circ$	$\Delta\bar{C}_{p_2}^\circ$
		$\text{cm}^3 \text{g}^{-1}$	$\text{cm}^3 \text{g}^{-1}$	$10^{-12} \text{cm}^2 \text{dyn}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$
T 10	—	—	—	—	272 ± 6	73
T 40	0.206	0.616	0.16	-6.8	278 ± 2	79
T 110	0.311	0.612	0.15	-6.6	259 ± 13	60
T 500	0.541	0.620	0.12	-5.2	—	—
T 2000	0.691	0.614	0.10	-4.5	202 ± 16	3

quadratic form of the molal concentration m to avoid the overemphasis of the data obtained in dilute region where the C_p values are less accurate.

All the results obtained in the present work are summarized in Table III, in which $\Delta\bar{C}_{p_2}^\circ$ is defined as $\Delta\bar{C}_{p_2}^\circ = C_{p_2}^\circ - C_{p_2}$ (pure state). As mentioned above, the values of $\bar{C}_{p_2}^\circ$ shown in Table III were calculated for the structural unit of the dextran molecule. The hypothetical value of the heat capacity of the structural unit of the dextran molecule in the pure state was estimated by modifying the method proposed by Dobratz.¹⁰ The estimated value is $199 \text{ J mol}^{-1} \text{ K}^{-1}$. This value permits the calculation of $\Delta\bar{C}_{p_2}^\circ$ given in the last column of Table III. The quantity $\Delta\bar{C}_{p_2}^\circ$ is a measure of the change in the water structure originating from the dissolution of solutes.

The monomer of the dextran molecule is glucose, for which the following values have been reported (the same system of units as in Table III is adopted):

\bar{v}_2°	ω	$C_{p_2}^\circ$	$\Delta C_{p_2}^\circ$
0.621	0.35, ⁹ 0.37 ¹¹	336 ⁷	109 ⁷

In Table III, the value of \bar{v}_2° remains constant within the limit of experimental error, and this value coincides with that for the glucose molecule shown above. The degree of polymerization has little effect on the partial specific volume of dextran in water. On the other hand, the amount of bound water calculated from the partial specific compressibility decreases with increasing molecular weight. It is reasonable to attribute the hydration of dextran is attributable to the hydrophilic OH group contained in the molecule. The decrease of the hydration water determined as the unit quantity of polymer as function of molecular weight of dextran may be due

to the decrease in the number of the free OH groups contacting directly the surrounding water molecules.

The values of $\Delta\bar{C}_{p_2}^\circ$ decrease as a result of the decrease in $\bar{C}_{p_2}^\circ$ values with molecular weight of dextran. A comparison of $\Delta\bar{C}_{p_2}^\circ$ of dextran with the corresponding value for glucose indicates that the change in the water structure caused by dissolution of one structural unit of the dextran molecule is smaller than in the case of glucose. In addition, the degree of this change decreases rapidly with increasing molecular weight of polymer, and for dextran T 2000, $\bar{C}_{p_2}^\circ$ and C_{p_2} (pure state) are nearly the same in magnitude.

The deviation from the linearity in the double-logarithmic plot of $[\eta]$ vs. M_w as shown in Figure 1, has been ascribed to the increased branching of dextran with increasing molecular weight. It may be considered that the branching effect can explain the variations of \bar{v}° and $\Delta C_{p_2}^\circ$ with molecular weight. First, we consider \bar{v}_2° . The variation of specific volume \bar{v}_2° , with molecular weight is a rather delicate problem. It has been shown¹² that the partial specific volume of a polymer may be expressed by the relation,

$$\bar{v}_2^\circ = \bar{v}_m + K/M_n$$

where K is a constant which is negative for polystyrene in benzene and positive for poly(methyl methacrylate) in benzene.¹² This relation holds for polystyrenes with different end-groups, but only for those having M_n below 4×10^4 .¹³ For comb-type polystyrenes with the same degree of branching and the branches of identical length, the values of \bar{v}_2° were independent of molecular weight.¹⁴ If these facts are considered, it is not certain whether the approximately constant values of \bar{v}_2° of dextran illustrated in Table III are related to the branching

of the polymer chain. Next, we consider $\Delta\overline{C}_{p_2}^\circ$. The increase of branching will decrease the portion of the polymer chain in direct contact with the solvent, thus giving rise to the decrease in the parameter $\Delta\overline{C}_{p_2}^\circ$. However, the interpretation in terms of branching does not go well with the results for ω . The reasons are as follows. As mentioned above, it is reasonable to assume that the amount of hydration determined in the present work corresponds to the bound water attracted by the hydrophilic group of OH. If one branching is produced in the polymer chain, one OH group is decreased, or a result of the formation of $-\text{O}-\text{C}-$ linkage, but at the same time one end group OH appears; The total number of OH groups in the polymer chain remains unchanged. Therefore, the effect of branching is not the only factor governing the molecular weight dependence of the physical parameters of aqueous solutions of dextran. In addition to branching, effects of the entanglement of polymer chains should also be taken into account: With increasing molecular weight, the entanglement of polymer chains increases. This effect produces i) a decrease in the number of free OH groups available for hydration and ii) weakening of the interaction between solute-solvent with the result that the degree of the structural change upon dissolution of unit structure of polymer decreases.

It seems to be more appropriate to attribute the molecular weight dependences observed in this study to the combination of branching and en-

tanglement of the polymer chains.

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