

## Partial Specific Compressibility of Dextran

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### Synopsis

The limiting partial specific compressibility (LC) of low molecular weight dextran in aqueous solution was determined by the measurements of ultrasonic velocity and density. The negative value of LC was ascribed to hydration. The amount of bound water calculated from LC and its temperature dependence were in accord with those of sugars in order of magnitude.

### Introduction

The limiting partial specific compressibility (LC) of a solute is a quantity obtained from the compressibility of the dilute solution at various concentrations by extrapolation to extreme dilution. In our previous paper,<sup>1</sup> it was shown that the magnitude of LC of linear polymers such as polystyrene and poly(vinyl acetate) in various solvents varies with their solvent power. In a good solvent, the magnitude of LC is of the order of the compressibility of liquid and positive.

On the other hand, the LC of hydrophilic solutes such as sugars<sup>2,3</sup> and starch<sup>4</sup> in the aqueous solutions was negative. In these solutions, some of the solvent are bound to the solute, and the decrease of free solvent molecules reduces LC to a negative value.

The purpose of this study is to present data on the LC of low molecular weight dextran, a hydrophilic, water-soluble polymer. Dextran is a branched, flexible polymer, and its solution properties are well known.<sup>5-7</sup> Studies on the compressibility of aqueous solutions of carbohydrates such as starch, dextrin, and glycogen have been reported by our colleagues.<sup>4,8,9</sup>

### Notation

The limiting partial specific compressibility of a solute is defined as

$$\bar{\kappa}_{20} = -(1/\bar{v}_{20}) (\partial\bar{v}_2/\partial p)_0 \quad (1)$$

where  $\bar{v}_2$  is the partial specific volume of the solute and the subscript zero refers to the value at infinite dilution. The method of obtaining the LC

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from the data of compressibility and density of the dilute solution was given in the previous paper.<sup>1</sup>

### Experimental

The compressibility (adiabatic) of the aqueous solution of dextran was determined by measuring the ultrasonic velocity and density. The ultrasonic interferometer used was similar to that reported previously.<sup>10</sup> The cell was made of stainless steel, and the ultrasonic frequency was 4 mcycle/sec. The density was determined with an Ostwald pycnometer.

Dextran was of clinical type, CL-2004, a product of Meito Sangyo Co. (Nagoya). The material had been prepared by cultures of *Leuconostoc mesenteroides*, subjected to the hydrolysis with hydrochloric acid, and fractionated with ethanol as precipitant. The molecular weight determined by the viscosity measurement was  $2.0 \times 10^5$ . The viscosity-molecular weight relation used here was

$$[\eta] = 6.1165 \times 10^{-4} M^{0.54} \quad (25^\circ\text{C.})$$

which had been determined by Inoue<sup>11</sup> from the osmotic pressure measurements at 25°C.

### Results and Discussion

The compressibility and density of aqueous solution of dextran were determined at 10, 20, 30, and 40°C. at concentrations of 0.02, 0.04, 0.06, 0.08, and 0.10 g./cc. solution. The plots of both  $(d - x)/d_1$  and  $\kappa/\kappa_1$  against the concentration were linear as in the previous report.<sup>1</sup> The calculated values of the partial specific volume and the LC are summarized in Table I.

TABLE I  
Limiting Partial Specific Compressibility, Partial Specific Volume, and Amount of Bound Water of Dextran in Aqueous Solution

Temp., °C.	$\bar{v}_{10}$ , cc./g.	$\bar{\kappa}_{20} \times 10^{12}$ , cm. <sup>2</sup> /dyne	$\omega$ cc./g.
10	0.60	-12.7	0.26
20	0.61 <sub>5</sub>	- 7.8	0.17
30	0.62	- 5.7	0.13
40	0.62	- 3.5	0.09

The existence of bound water of sugars in aqueous solution has been confirmed by various methods. Miyahara and Shio<sup>2</sup> and Shio<sup>3</sup> have determined the amount of bound water of various sugars by ultrasonic velocity measurements, and hydration of a similar order of magnitude has been obtained from the activity data by Miyahara<sup>12</sup> and Robinson and Stokes.<sup>13</sup> An estimate of the amount of bound water from viscosity and diffusion coefficient data has also been reported by Edward.<sup>14</sup> It is highly probable that the segments of dextran molecule bear some amount of bound water in aqueous solution, which makes the LC negative.

In the previous paper,<sup>1</sup> it was concluded that the linear chain polymer molecule stretches freely in a good solvent, and each segment behaves like micromolecular solute, forming a liquid mixture with the neighboring solvent molecules. Consequently, the LC of such a polymer shows a rather high value, comparable to that of a micromolecular solute in an organic liquid mixture.

Water is a good solvent for dextran, and so the dextran molecule also stretches in the aqueous solution. To account for the negative value of LC, therefore, a different behavior of the segments should be assumed. The movement of the segments of dextran molecule is not so free as that of a free chain polymer in organic solvent, owing to the burden of the bound water, and the molecule cannot behave like solute molecules in the organic liquid mixtures. The hydrated segments should be treated as solid particles.

Shiio<sup>3</sup> has estimated the amount of hydration of sugars by assuming that the compressibility of solute molecule is zero. If we adopt this assumption, we can estimate the amount of bound water of dextran by using the equation given in the previous paper,<sup>1</sup> which reduces to

$$\omega = -\bar{v}_{20}\kappa_{s0}/(\kappa_1 - \kappa_h) \quad (2)$$

where  $\omega$  is the amount of bound water (in cubic centimeters per gram of the solute), and  $\kappa_1$  and  $\kappa_h$  are the compressibilities of pure water and the bound water, respectively.

The amount of bound water of dextran calculated is shown in the last column of Table I. In the calculation, the compressibility of the bound water was assumed to be  $18 \times 10^{-12}$  cm.<sup>2</sup>/dyne, as suggested by Shiio.<sup>3</sup> The amount of hydration of dextran was, as is seen in the table, slightly smaller than that of sugars reported by Shiio. This is probably due to the assumption that the molecule is incompressible. The compressibility of the dextran molecule might be higher than zero as a result of some intramolecular hydrogen bonding.

The amount of hydration of sugars decreased with increasing temperature, as has been shown by Shiio<sup>3</sup> and Miyahara.<sup>12</sup> The temperature dependence of hydration of dextran shown in Table I is in accord with that of sugars. This result suggests that the heat of hydration of dextran is similar in order of magnitude to that of sugars.

As far as the compressibility of dilute solution is concerned, the dextran molecule can be treated as a motionless necklace, the beads of which are the segments bearing bound water.

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### Résumé

La compressibilité partielle spécifique limite (LC) du dextrane de bas poids moléculaire et en solution aqueuse, a été déterminée par des mesures de densité et de vitesse ultrasonique. On a expliqué la valeur négative de LC par hydratation. La quantité d'eau liée calculée au départ de LC et sa dépendance de la température correspondent, en ordre de grandeur, avec celles des sucres.

### Zusammenfassung

Die partielle spezifische Grenzkompessibilität (LC) von niedrigmolekularem Dextran in wässriger Lösung wurde durch Ultraschallgeschwindigkeits- und Dichtemessungen bestimmt. Der negative Wert von LC wird der Hydratation zugeschrieben. Die aus LC und seiner Temperaturabhängigkeit berechnete Menge an gebundenem Wasser war in grössenordnungsmässiger Übereinstimmung mit derjenigen von Zuckern.

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