# Unperturbed Dimensions and the Theta Temperature of Dextran in Aqueous Solutions

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**ABSTRACT:** Intrinsic viscosity measurements were carried out on dextran samples (of different molecular weights) in aqueous solutions at 25, 28, 31, 34, 37, 40, and 43°C. The extrapolation methods were used for the data; they gave unperturbed dimensions,  $K_0$ , of the chain. The unperturbed root-mean-square end-to-end distance  $\langle r^2 \rangle_0^{1/2}$  calculated for the polymer samples in water indicate that the polymer coils are slightly contracted in this solvent as the temperature is increased. The long-range interaction parameter, B, was also determined. In aqueous dextran solutions, this showed a significant decrease in the long-range interactions between 25 and 43°C. The values of  $\Theta = 317.82$  and 316.57 K were obtained from the temperature dependence of the interaction parameter B in the Kurata–Stockmayer–Fixman and Berry equations. Calculated values were interpreted mainly on the basis of hydrogen-bond formation between polymer segments and dextran–water molecules in solution. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 871–876, 1999

Key words: dextran; aqueous solutions; unperturbed dimensions; theta temperature

#### **INTRODUCTION**

Dextran is a water-soluble polymer and has importance in different chemical technologies. Despite keen interests in the solution properties<sup>1-4</sup> of dextran, few investigations have been made on the thermodynamics of polymer solutions. Hefford<sup>5</sup> studied the phase behavior of dextran in aqueous solutions. Haynes and coworkers<sup>6</sup> examined aqueous solutions of dextran to obtain virial coefficients and calculated liquid–liquid equilibria in ternary systems from the constituent binary systems. Diamond and Hsu<sup>7</sup> found a semiempirical thermodynamic expression in a poly(ethylene glycol)/dextran aqueous two-phase system.

The theta temperature is the temperature at which, for a given polymer–solvent system, the polymer exists in its unperturbed dimensions and can be determined by colligative property measurements or cloud-point temperature measurements.<sup>8–10</sup> The aim of this work was to study the unperturbed dimensions, hydrodynamic expansion, and long-range interaction behavior of dextran in dilute solutions between 25 and 43°C by intrinsic viscosity measurements and to determine the theta temperature of the polymer in aqueous solutions.

### **EXPERIMENTAL**

The four polymer samples studied in this work were obtained from Pharmacia Fine Chemicals AB (Uppsala, Sweden). The molecular weight characteristics were determined by Pharmacia (except in T 70) and the number-average molecular weights of T 40, T 110, and T 500 are given in Table I. All dextran samples were dried and stored in a dessicator over  $CaCl_2$  and were used without further purification.

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Sample	Number-Average Molecular Weight (g/mol)
T40 <sup>a</sup>	29,500
T70 <sup>b</sup>	46,800
T110 <sup>a</sup>	74,000
T500 <sup>a</sup>	191,500

<sup>a</sup> Determined by Pharmacia Fine Chemicals AB, Uppsala, Sweden,

<sup>b</sup> Determined by a Knauer membrane osmometer in aqueous solution at room temperature.

Deionized and bidistilled water was used to prepare the aqueous dextran solutions. The viscosity measurements were performed at 25, 28, 31, 34, 37, 40, and 43°C, using an Ubbelohde-type capillary viscometer, and all the polymer solutions were used immediately after preparation. The temperature of the thermostat was controlled to within  $\pm 0.1$ °C, the efflux times were reproducible to  $\pm 0.2\%$ , and the flow times were measured with an accuracy of  $\pm 0.1$  s. In the molecular weight range investigated, shear rate effects were assumed to be negligible. The concentration dependence of the viscosity of dilute dextran solutions was followed by the well-known Huggins equation:

$$\eta_{\mathrm{sp}/c} = [\eta] + k_H [\eta]^2 c$$

The intrinsic viscosities  $[\eta]$  were obtained from plots of the  $\eta_{sp/c}$  ratio against the polymer concentration with subsequent extrapolation to infinite dilution. The intrinsic viscosity-molecular weight relationships at these seven temperatures were determined with the well-known Mark-Houwink equation,  $[\eta] = KM^a$ , and the constants K and a values are given in Table II.

### **RESULTS AND DISCUSSION**

The unperturbed dimension parameter,  $K_0$ , independent of solvent, temperature, and molecular weight of the polymer, can be calculated by extrapolation methods.<sup>11</sup> Information on the unperturbed dimensions, starting from the viscosity results, was obtained from the Kurata–Stockmayer–Fixman (KSF) equation<sup>12,13</sup>:

Table IIMark-Houwink Constants of DextranSamples in Aqueous Solutions

Temperature (K)	$K  imes 10^4 \; ({\rm dL/g})$	а
298	7.337	0.533
301	7.455	0.529
304	8.268	0.519
307	8.474	0.515
310	8.518	0.513
313	8.860	0.508
316	9.462	0.500

$$[\eta]M^{-1/2} = K_0 + 0.51B\Phi_0 M^{1/2} \tag{1}$$

where

$$K_0 = [\eta] \Theta / M^{1/2} = \Phi_0 (\langle r^2 \rangle_0 / M)^{3/2}$$
(2)

 $K_0$  and B are parameters for short-range and long-range interactions, respectively,  $\langle r^2 \rangle_0^{1/2}$  represents the root-mean-square end-to-end distance of the unperturbed polymer chain, and  $\Phi_0$  is Flory's universal constant (in this study, the value of  $2.1 \times 10^{23} \text{ mol}^{-1}$  was used). The plot of  $[\eta] M_n^{-1/2}$  versus  $M_n^{1/2}$  yields a straight line, the intercept being  $K_0$  and the slope being characteristic of polymer–solvent interactions (Fig. 1). It is also possible to determine the intrinsic viscosity  $[\eta]\Theta$  at the theta temperature and the root-meansquare end-to-end distance of the polymer at the



**Figure 1** KSF plot for the dextran fractions at the 25–43°C temperature range.

Dextran	$[\eta] 25^{\circ} C (dL g^{-1})$	$[\eta] \theta (dL g^{-1})$	$\alpha_{\eta}$	$\langle r^2  angle_0^{1/2}  imes 10^7 ~( ext{cm})$
T40	0.178	0.170	1.015	2.88
T70	0.226	0.214	1.018	3.63
T110	0.288	0.269	1.023	4.56
T500	0.482	0.433	1.037	7.34
	$[\eta] 28^{\circ} \text{C} (\text{dL g}^{-1})$			
	0.175	0 168	1.019	2.86
T40 T70	0.175	0.100	1.015	2.00
T110	0.222	0.212	1.015	5.00
1110 TE00	0.200	0.200	1.021	4.00
1900	0.471	0.428	1.032	7.30
	$[\eta]$ 31°C (dL g <sup>-1</sup> )			
T40	0.173	0.168	1.009	2.87
T70	0.222	0.212	1.013	3.60
T110	0.279	0.267	1.014	4.54
T500	0.459	0.429	1.023	7.31
	$[\eta] 34^{\circ}C (dL g^{-1})$			
<b>Τ</b> 40	0.171	0 167	1 007	2.87
T40 T70	0.171	0.107	1.007	2.01
T110	0.210	0.211	1.000	5.00
T500	0.274	0.205 0.427	1.011	4.54
	0.110	0.121	1.010	1.01
	$[\eta]$ 37°C (dL g <sup>-1</sup> )			
T40	0.168	0.165	1.006	2.85
T70	0.213	0.208	1.008	3.59
T110	0.269	0.262	1.009	4.52
T500	0.439	0.422	1.013	7.27
	$[\eta] 40^{\circ} C (dL g^{-1})$			
T40	0 166	0 164	1 004	2.85
T70	0.209	0.207	1.003	3 59
T110	0.264	0.260	1.005	4 52
T500	0.429	0.418	1.009	7.27
	$[\eta] 43^{\circ} C (dL g^{-1})$			
<b>T</b> 40	0 169	0 169	1 000	0.00
140 T70	0.100	0.100	1.000	2.00 9 EC
I (U TT110	0.200	0.200	1.001	0G.G
1110	0.259	0.258	1.001	4.48
1500	0.416	0.415	1.001	1.22

Table IIICalculated Data for Dextran Solutions from Intrinsic ViscosityMeasurements in the Temperature Range of 25-43°C

unperturbed state using eq. (2). The intrinsic viscosity may be expressed in the form

where  $\alpha_{\eta}$  is the hydrodynamic expansion factor. Experimentally determined  $[\eta]$  values at various temperatures and calculated  $[\eta]\Theta$ ,  $\alpha_{\eta}$ , and  $\langle r^2 \rangle_0^{1/2}$  values are given in Table III.

$$[\eta] = [\eta] \Theta \alpha_{\eta}^{3} \tag{3}$$



**Figure 2** Berry plot for the dextran fractions at the 25–43°C temperature range.

Another extrapolation method was reported by Berry<sup>14</sup>:

$$[\eta]^{1/2}M^{-1/4} = K_0^{1/2} + 0.42K_0^{1/2}B\Phi_0 M[\eta]^{-1} \quad (4)$$

Similar to KSF behavior, a straight-line plot of  $[\eta]^{1/2}M_n^{-1/4}$  versus  $M_n[\eta]^{-1}$  was obtained, the intercept being  $K_0^{1/2}$  and the slope also being characteristic of polymer–solvent interactions (Fig. 2).

Unperturbed dimension and long-range interaction parameters calculated by both extrapolation methods are given in Table IV. However, it would be better to evaluate the viscosity data given in Table III before explaining these parameters in detail. It is known that dextran forms hydrogen bonds with water molecules in its aqueous solutions.<sup>4</sup> These bonds break with increasing

3.174

9.50

temperature, and the hydrodynamic volume of the polymer decreases. This is in accordance with decrease in the intrinsic viscosity values. Still, it is interesting to observe that no significant difference exists between the  $[\eta]$  and  $[\eta]\Theta$  obtained from eq. (2). Similarly,  $\langle r^2 \rangle_0^{1/2}$  does not change significantly with increasing temperature, but an 18°C temperature increment causes decreases in the  $\alpha_n$  values. The highest decrease is observed with the highest molecular weight (T 500) of the dextran sample. According to eq. (3),  $\alpha_n = 1$  only when  $[\eta]\Theta = [\eta]$ . On the other hand,  $\alpha_n$  values obtained at 43°C are equal to 1 or very nearly so. Up to this point, the theta temperature of dextran in water is expected to be 43°C or slightly above this in view of the calculated values.

Another consideration parallel to this idea is true again with respect to the viscosity values. At a 25–43°C temperature interval, a, the superscript in the Mark–Houwink relationship, decreases with increasing temperature. At the theta temperature, it is known that a = 0.5. Besides, the Mark–Houwink constant K also increases with increasing temperature and approaches the unperturbed dimension parameter  $K_0$  evaluated by extrapolation methods.

The  $K_0$  values, obtained from both extrapolation techniques, are in accordance with each other (Table IV). With increasing temperatures, the decrease in  $K_0$  values is quite obvious and also the difference between the Mark–Houwink constant, K, at the highest temperature, and the unperturbed dimension parameter,  $K_0$ , obtained from extrapolation methods, is about  $4 \times 10^{-6}$ .

Considering the relationship between the temperature increment and reduction in  $K_0$ , under theta conditions (or as commonly used at unper-

0.01

KSF Berry  $1/T \times 10^3$  $K_0 \times 10^4$  ${K_0 imes 10^4 \ ({
m dL g}^{-1})}$  $(K^{-1})$  $(dL g^{-1})$  $B \, imes \, 10^{30}$  $B \times 10^{30}$ 3.3559.90 2.379.88 1.579.79 9.76 1.393.3212.053.2889.81 1.489.83 0.89 3.2569.76 1.029.74 0.66 3.2259.640.849.610.583.194 9.560.519.530.37

0.33

9.50

Table IVCalculated Thermodynamic Parameters for Aqueous DextranSolutions at Various Temperatures



**Figure 3** Plot of the interaction parameter B as a function of the reciprocal of the absolute temperature (KSF).

turbed dimensions), segmental interactions become attractive. Considering the structure of dextran, one can easily see that the polymer has ring-oxygen and bridge-oxygen atoms in each repeating unit besides the three hydroxyl groups in the ring structure. It is strongly expected that hydrogen bonding will form between hydroxyl groups with hydrogen acceptor-donor characteristics and ether oxygen, showing hydrogen-acceptor behavior. Obviously, these hydrogen bonds will break at increased temperature and hydrophobic interactions between polymer segments will be more dominant. Finally, due to these interactions, a contraction will be observed in the polymer coil. This change can also be followed from temperature-intrinsic viscosity behavior.

The long-range interaction parameter, B, is defined as the magnitude expressing polymer– solvent interactions. It is quite well known that dextran forms hydrogen bonds both with water<sup>2,4</sup> and some conventional polar solvents.<sup>1,15</sup> In this study, a significant drop was observed in the longrange interaction parameters (Table IV) obtained by both of the extrapolation methods. One can evaluate this large difference in terms of a temperature increment causing the break of hydrogen bonds between polymer and water molecules.

The temperature dependence of B, as suggested by Flory,<sup>16</sup> is given by

$$B = B_0(1 - \Theta/T) \tag{5}$$

where  $B_0$  is a constant, independent of temperature, which can be found from the temperature of the second virial coefficient near the theta temperature. The plots of *B* obtained from KSF and Berry equations against the reciprocal of the temperature according to eq. (5) are shown in Figures 3 and 4, respectively. In these figures, the straight lines through the seven experimental points are given by the following equations:

(i) According to the *B* values obtained from the KSF equation,

$$1.1084 \times 10^{-26} = -(-3.4879 \times 10^{-29})\Theta$$
(6)

$$\Theta = 317.82 \text{ K}$$
 (7)

(ii) According to the *B* values obtained from he Berry equation,

$$7.9080 \times 10^{-27} = -(-2.4981 \times 10^{-29})\Theta \qquad (8)$$

$$\Theta = 316.57 \text{ K} \tag{9}$$

In this work, however, the theta temperature of the dextran-water system was lower than that of some other water-soluble polymers in their aqueous solutions (Table V). When polyvinylpyrrolidone (PVP) and poly(ethylene oxide) (PEO) are considered, respectively, hydrophillic car-



**Figure 4** Plot of the interaction parameter *B* as a function of the reciprocal of the absolute temperature (Berry).

System	Θ (K)	Method
Dextran-water	317-318	KSF and Berry
Poly(ethylene oxide)-water <sup>17-19</sup>	369-373	Cloud-point temperature measurements <sup>a</sup>
Poly(ethylene oxide)-water <sup>20</sup>	381	KSF
Polyvinylpyrrolidone-water <sup>9</sup>	$420\pm7$	Cloud-point temperature measurements <sup>a</sup>
Polyvinylpyrrolidone–water <sup>21</sup>	$413\pm5$	KSF
Polyvinylpyrrolidone-water <sup>22</sup>	404	Cloud-point temperature measurements <sup>b</sup>

Table V Theta Temperatures of Some Water-Soluble Polymers

<sup>a</sup> In the presence of inorganic salts.

<sup>b</sup> In the presence of  $Na_2\bar{C}O_3$ .

bonyl in the lactam ring of PVP and, again, hydrophillic ether oxygen of PEO can be seen. Experimental studies have proved that these polymers form hydrogen bonding with water molecules due to these characteristics.<sup>23-26</sup> The destruction of polymer–solvent interaction and, consequently, the dominance of hydrophobic interactions between polymer segments at unperturbed dimensions may only be valid at high temperatures for these two water–soluble polymers.

In the dextran structure, as previously discussed, each repeating unit has hydrogen-bonding donor and acceptor groups very similar to the water structure. In other words, polymersolvent interactions and interactions between polymer segments occur almost at the same level. It is useful to keep in mind that the superscript, a, in the Mark-Houwink equation was found as 0.533 at 25°C. Of course, this behavior gives hints about the solvent character of the solvent employed for dextran. Basedow and coworkers<sup>1</sup> claimed that dimethyl sulfoxide, a strong hydrogen acceptor, may be a better solvent for dextran than is water on the basis of the enthalpy values evaluated for the solutions of the polymer in various solvents.

As a conclusion, referring to hydrodynamic magnitudes, it has been observed that interactions, both between polymer segments and polymer-solvent molecules, are in competition with each other. Polymer-solvent interaction seems to be a bit more dominant, while interactions between polymer segments may also be effective, and with increasing temperature, it is most probable that both types of interactions may be suppressed.

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