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Unperturbed molecular dimensions and the theta temperature of dextran in dimethylsulfoxide (DMSO) solutions

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Summary

The unperturbed molecular dimensions of dextran samples have been determined in dimethylsulfoxide (DMSO) solutions from intrinsic viscosity measurements at different temperatures. The unperturbed dimension parameter, K_o , has been calculated from extrapolation methods.The unperturbed root-mean-square end-to-end distance, $<r^2>_o^{1/2}$, found for the polymer samples in DMSO solutions, indicate that the polymer coils are contracted. This distance varies from 3.25 x 10^{-7} cm to 2.94 x 10^{-7} cm for the sample T 40 and from 8.28 x 10^{-7} cm to 7.48 x 10^{-7} cm for the sample T 500, in the chosen solvent as the temperature is raised from 25°C to 45°C. In the system of dextran/DMSO, the long-range interaction parameter, B, was also determined and a significant decrease is observed between 25°-45°C. The theta temperatures, Θ, were obtained as Θ = 327.25 K, Θ = 327.41 K and Θ = 323.38 K from the temperature dependence of the interaction parameter in Kurata-Stockmayer-Fixman, Berry and Inagaki-Suzuki-Kurata equations, respectively.

Introduction

Dextran is the collective name of a large class of polysaccharides composed exclusively of D-glucose units. Dextran is soluble in water and some conventional polar solvents (i.e. ethylene glycol, glycerol, formamid and DMSO etc.) and has important technological applications. The dextran polymer has ring-oxygen and bridge oxygen atoms in each repeating unit besides the hydroxyl groups in the ring structure. Considering the structure of dextran, it is expected that molecular association will form between the polymer segments and solvent molecules by hydrogen bonding (1). Effects of certain organic additives on the molecular association of dextran (2) and periodate-oxidised dextran (3) have been previously studied by viscosimetric measurements in aqueous solutions.

Theta temperature,Θ,(Flory temperature), for a certain polymer-solvent pair, is the temperature at which the polymer chains assume their unperturbed dimensions, the intermolecular interactions vanish and segmental interactions become attractive. The theta temperature can be determined by light scattering and osmotic pressure measurements, turbidity or cloud- point temperature measurements (4,5) and the long-range interaction-temperature relationship (6,7). But, no references have been found in the literature relating the theta temperature of the system dextran/DMSO.

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In extrapolation methods (8), in addition to the unperturbed dimension parameter, it is also possible to follow the unperturbed root-mean-square end-to-end distance and the long-range interactions by intrinsic viscosity values at different temperatures.

Experimental

The polymer samples studied in this work were obtained from Pharmacia Fine Chemicals AB Uppsala, Sweden. The molecular weight characteristics are determined by Pharmacia (except in T 70) and are given as, for T 40 sample ; M_n= 29 500 g mol^{-1}, T 110 sample ; M_n= 74 000 g mol^{-1} and T 500 sample ; M_n= 191 500 g mol^{-1}. The number average molecular weight of T 70 dextran sample is determined as M_n= 46 800 g mol^{-1} by Knauer membran osmometer in aqueous solution at room temperature.

The solvent, dimethylsulfoxide (DMSO) was an analytical grade and obtained from British Drug House (BDH). All solutions were prepared by weighing the polymer samples and the polymer samples were used without further purification.

The viscosity measurements were performed at 25°, 30°, 35°, 40° and 45°C, using an Ubbelohde type of capillary viscometer. The temperature of the thermostate was controlled within a range of ± 0.1°C and the flow times were measured with a digital accuracy of ± 0.1 s. The concentration-dependence of the viscosity results of dilute polymer solutions (in 0.4-0.2 g dL^{-1} concentration range) was followed by the well-known Huggins equation.

Results and discussion

Viscosity characteristics

The intrinsic viscosity ($[\eta]$) - molecular weight (M_n) relationship is given by Mark-Houwink equation ($[\eta] = KM_n^a$) and the Mark-Houwink constants K and a for dextran samples at various temperatures were found as ;

$$T = 25^oC \qquad K = 1.05 \times 10^{-3}\ (dL\ g^{-1}) \qquad a = 0.533 \qquad (1)$$

$$T = 30^oC \qquad K = 1.07 \times 10^{-3}\ \text{"} \qquad a = 0.525 \qquad (2)$$

$$T = 35^oC \qquad K = 1.04 \times 10^{-3}\ \text{"} \qquad a = 0.519 \qquad (3)$$

$$T = 40^oC \qquad K = 1.02 \times 10^{-3}\ \text{"} \qquad a = 0.517 \qquad (4)$$

$$T = 45^oC \qquad K = 9.19 \times 10^{-3}\ \text{"} \qquad a = 0.514 \qquad (5)$$

The decrease in K values and also in the superscript, a , in the Mark-Houwink relation, can be noticed easily from 25°C to 45°C. This observation would better be explained by discussing the structure and the interactions of the polymer in the absence and the presence of solvent. In the dextran structure, the polymer has hydrogen acceptor oxygen (ring- and bridge-) atoms and hydrogen acceptor and donor three hydroxyl groups in each repeating unit. It is strongly expected that hydrogen bonding will occur between these groups and these interactions will be disturbed at increased temperatures. In the presence of a solvent, polymer-solvent interactions will also arise and be affected by temperature changes. The solvent, DMSO, used in this study is a hydrogen acceptor. It is known that, Mark-Houwink constants both depend on the nature of solvent and temperature.Considering the theta temperature-Mark-Houwink superscript relationship, at theta temperature, constant **a** is equal to 0.5. It is interesting to observe the decrease in the superscript **a** with temperature. Considering the decrement in the **a** values, the theta temperature of dextran in DMSO solution is expected to be at around 50°-55°C temperature range. This stipulation has been also supported with the viscosimetric K values in the same temperature range. This constant is found as 1.05 x 10^{-3} dLg^{-1} at 25°C,but, it is dropped to 9.19 x 10^{-4} dLg^{-1} at 45°C , and very close to the unperturbed dimension parameter,K_o, evaluated by extrapolation methods (except in Inagaki-Suzuki-Kurata equation). Up to this point, referring to viscosimetric characteristics, it was observed that molecular dimension-temperature relationship or interactions (mainly hydrogen-bond formation) between polymer segments and polymer-solvent molecules are in competition with each other.

Unperturbed dimensions

It is known that the unperturbed dimension parameter, K_o, is independent of temperature, molecular weight of the polymer and solvent depending only on the short-range interactions. The information on unperturbed dimensions has been found from extrapolation methods by viscosimetrically determined intrinsic viscosity values. In the present study, Kurata-Stockmayer-Fixman (9,10) Burchard(11) equation (KSFB),

$$[\eta]\, M^{-1/2} = K_o + 0.51\, B\, \Phi_o M^{1/2} \qquad (6)$$

and the relationship between K_o and $< r^2>_o$ is given by

$$K_o = [\eta]_\Theta / M^{1/2} = \Phi_o\, (< r^2>_o/M)^{3/2} \qquad (7)$$

and Berry (12) equation,

$$[\eta]^{1/2} M^{-1/4} = K_o^{1/2} + 0.42\, K_o^{1/2}\, B\, \Phi_o\, M\, [\eta]^{-1} \qquad (8)$$

and, Inagaki-Suzuki-Kurata (13) equations (ISK),

$$[\eta]^{4/5} M^{-2/5} = 0.786\, K_o^{4/5} + 0.454\, K_o^{2/5}\, B^{2/3}\, \Phi_o^{2/3}\, M^{1/3} \qquad (9)$$

have been used for the calculation of polymer dimensions.

In these extrapolation methods, B is the parameter for long-range interactions, $< r^2>_o^{1/2}$ represents root-mean-square end-to-end distance of unperturbed polymer chain and Φ_o is Flory's universal constant (in this study the value of 2.1 x 10^{23} mol^{-1} is used). The plots of $[\eta]M_n^{-1/2}$ vs $M_n^{1/2}$(KSFB),$[\eta]^{1/2}M_n^{-1/4}$ vs M_n $[\eta]^{-1}$(Berry) and $[\eta]^{4/5}$ $M_n^{-2/5}$

vs $M_n^{1/3}$ (ISK) yielded straight lines, where the intercept being K_o and the slope characterising the polymer-solvent interactions (Figs 1, 2 and 3).

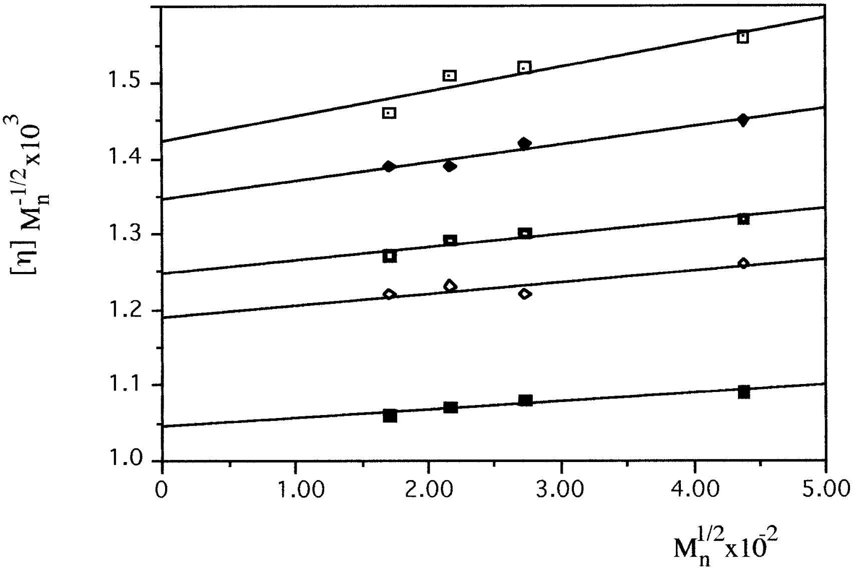

Figure 1. Kurata-Stockmayer-Fixman-Burchard plot for dextran fractions at different temperatures, ▣ 25°, ◆ 30°, ◘ 35°, ◇ 40°, ■ 45° C.

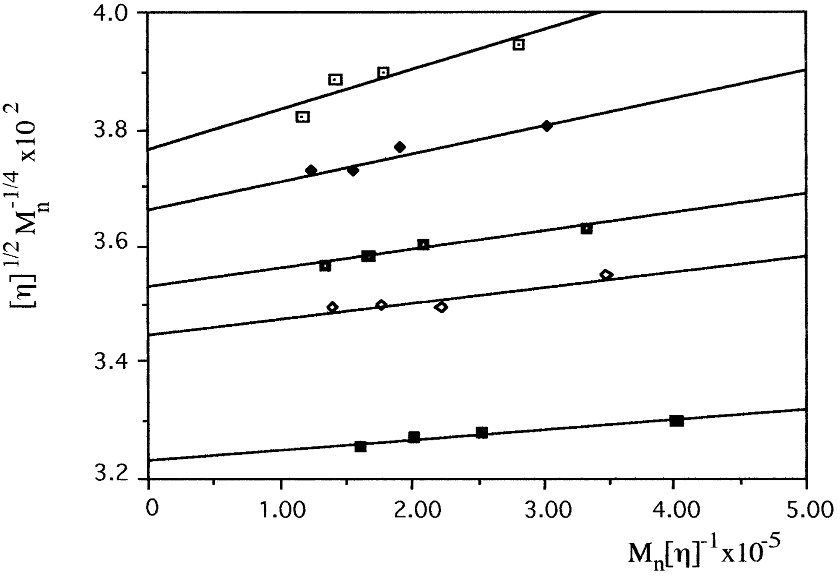

Figure 2. Berry plot for dextran fractions at different temperatures, ▣ 25°, ◆ 30°, ◘ 35°, ◇ 40°, ■ 45° C.

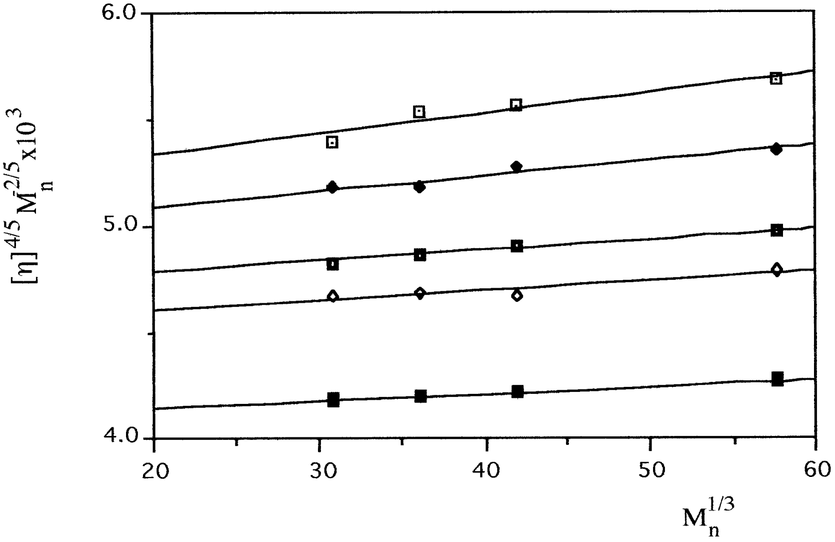

Figure 3. Inagaki-Suzuki-Kurata plot for dextran fractions at different temperatures, ⊡ 25°, ◆ 30°, ▣ 35°, ◇ 40°, ■ 45 °C.

One can possibly determine the intrinsic viscosity, $[\eta]\ \Theta$, at the theta temperature and also the root-mean-square end-to-end distance of the polymer at the unperturbed state using equation 7. The intrinsic viscosities, at the studied temperatures and the theta temperature, including the hydrodynamic expansion factor, α_η ,can be expressed in the form;

$$[\eta] = [\eta]\ \Theta\ \alpha\eta^{3} \qquad (10)$$

Experimentally determined $[\eta]$ values at different temperatures (25°,30°,35°,40° and 45°C) and the calculated $[\eta]\ \Theta$, α_η and $< r^2>_o^{1/2}$ values are given in Table 1. In Table 2, unperturbed dimensions and long-range interaction parameters are presented, found by extrapolation methods.

The unperturbed dimension parameters calculated from Kurata-Stockmayer-Fixman-Burchard and Berry equations are in great accordance with each other and the decrease in K_o values at increasing temperatures is quite obvious with these extrapolation techniques. An other observation is the long-range interaction-temperature behaviour.As can be seen from Table 2, at increasing temperatures, the decrease in B values is significant. Of course, this decrement in terms of temperature increment result in the rupture of polymer-solvent interactions, i.e., hydrogen-bonds between dextran and DMSO molecules. It is generally known that the distruption of hydrogen-bond formation decreases with temperature and the behaviour of dextran/DMSO system seems to be usual with this respect. It should be noted that the interactions may also occur between the polymer segments themselves (the structure of the polymer was presented previously). At low temperatures, the interactions between polymer segments seems to be a bit more dominant than the polymer-solvent interactions. At low temperatures, DMSO is not capable of destroying interactions between polymer segments.

Table 1. Calculated data for dextran/DMSO solutions from intrinsic viscosity measurements in the temperature range of 25°-45°C.

		$[\eta]_\Theta$ (dLg^{-1})	α_η	$< r^2 >_0^{1/2}$ x10^7 (cm)
Dextran	$[\eta]_{25^\circ C}$			
T40	0.251	0.244	1.009	3.25
T70	0.327	0.307	1.021	4.09
T110	0.414	0.386	1.023	5.14
T500	0.683	0.621	1.032	8.28
Dextran	$[\eta]_{30^\circ C}$			
T40	0.239	0.232	1.009	3.19
T70	0.301	0.292	1.010	4.02
T110	0.386	0.367	1.017	5.06
T500	0.634	0.591	1.024	8.13
Dextran	$[\eta]_{35^\circ C}$			
T40	0.219	0.215	1.006	3.11
T70	0.278	0.270	1.010	3.92
T110	0.354	0.340	1.013	4.93
T500	0.578	0.547	1.018	7.93
Dextran	$[\eta]_{40^\circ C}$			
T40	0.210	0.204	1.010	3.06
T70	0.265	0.257	1.010	3.86
T110	0.332	0.324	1.008	4.85
T500	0.551	0.521	1.019	7.80
Dextran	$[\eta]_{45^\circ C}$			
T40	0.182	0.180	1.004	2.94
T70	0.231	0.227	1.006	3.70
T110	0.293	0.286	1.008	4.65
T500	0.477	0.459	1.013	7.48

Table 2. Calculated thermodynamic parameters for dextran/DMSO solutions.

	KSFB		Berry		ISK	
T (°C)	$K_o x10^3$ (dLg^{-1})	$Bx10^{30}$ (cm^3)	$K_o x10^3$ (dLg^{-1})	$Bx10^{30}$ (cm^3)	$K_o x10^3$ (dLg^{-1})	$Bx10^{30}$ (cm^3)
25	1.42	3.05	1.42	2.02	1.86	20.1
30	1.35	2.24	1.34	1.47	1.77	13.5
35	1.25	1.59	1.25	1.01	1.66	8.28
40	1.19	1.36	1.19	0.99	1.58	7.43
45	1.05	0.98	1.05	0.61	1.39	4.89

The fact that K_o values decrease with increasing temperature in the 25°-45°C range, indicates that the interactions between polymer segments, via hydrogen-bond formation may be destroyed.

It is also possible to determine the polymer-solvent interactions from viscosity results, hydrodynamic expansion factor and end-to-end distance changes. Intrinsic viscosity is a measure of the hydrodynamic volume of the polymer in solution. Temperature increase causes a decrease in the intrinsic viscosity values. It is interesting that no significant difference exists between $[\eta]$ and $[\eta]\ \Theta$ values for dextran samples, especially at high temperatures. Hydrodynamic expansion factor, α_η , measures the intensity of the thermodynamic interactions. According to equation 10, $\alpha_\eta = 1$ only for $[\eta] = [\eta]\ \Theta$. On the other hand, α_η values obtained at 45°C are nearer to one. Similarly, end-to-end distance, $< r^2>_o^{1/2}$, decreases with temperature. Referring to hydrodynamic magnitutes,the contraction of the polymer coil has been observed at increasing temperatures.

The temperature dependence of long-range interaction parameter, as suggested by Flory (14), is given by ;

$$B = B_o (1 - \Theta /T) \tag{11}$$

where B_o is a constant, independent of temperature ,and Θ is the theta temperature of the polymer. The plots of B obtained from Kurata-Stockmayer-Fixman-Burchard ,Berry and Inagaki-Suzuki-Kurata equations against reciprocal of the temperature, according to equation 11, are shown in Figure 4. The theta temperatures were found as ; Θ = 327.25 K (according to B values obtained from Kurata-Stockmayer-Fixman-Burchard equation), Θ = 327.41 K (according to B values obtained from Berry equation) and Θ = 323.38 K (according to B values obtained from Inagaki-Suzuki-Kurata equation) for dextran in DMSO solutions.

In the light of hydrodynamic and thermodynamic magnitutes, it has been observed that the interactions, mainly the hydrogen-bond formation, both between the polymer segments and polymer-DMSO molecules are in competition with each other. Interactions between polymer and DMSO molecules seem to be more dominant than those interactions between the polymer segments. Temperature increment is an effective force to destroy both types of interactions,as for the behaviour of dextran-water system (7).

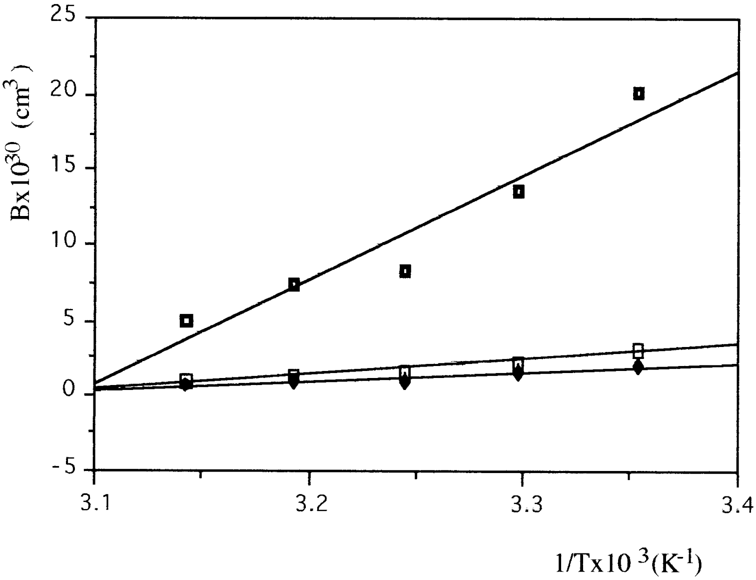

Figure 4. Plot of the interaction parameter B (□ Kurata-Stockmayer-Fixman-Burchard, ◆ Berry, ■ Inagaki-Suzuki-Kurata) as a function of the reciprocal of the absolute temperatures.

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