Biophysical Chemistry 16 (1982) 269–273
Elsevier Biomedical Press

ACTIVATION ENTHALPY OF DIFFUSION FOR WELL FRACTIONATED DEXTRANS IN AQUEOUS SOLUTIONS

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Received 31st March 1982
Revised manuscript received 14th July 1982
Accepted 28th July 1982

Key words: Activation enthalpy; Dextran; Interdiffusion; Self-diffusion

Interdiffusion coefficients have been determined for seven well defined dextran fractions in aqueous solutions at 20, 25, 30 and 35°C. For dextrans with number average molecular weights ($\overline{M}_n$) greater than about 20000, a plot of the apparent activation energy of diffusion (E_D) against $\overline{M}_n$ is given by: $E_D = 2.763 \times 10^{-5}\ \overline{M}_n + 3.38$. Similarly, for weight average molecular weight ($\overline{M}_w$): $E_D = 1.889 \times 10^{-5}\ \overline{M}_w + 3.61$. The extrapolated E_D values (3.38 and 3.61) are in reasonably good agreement with published data for the activation energy of self-diffusion for water.

1. Introduction

Dextran is the collective name of a large class of extracellular bacterial polysaccharides whose main molecular chain consists of anhydro-D-glucopyranose units linked predominantly by α-1,6-glucosidic bonds. The macromolecules of various dextran preparations may contain also various quantities of α-1,2-, α-1,3- and α-1,4-glucosidic bonds, by means of which side chains are usually attached to the main chain. Aqueous solutions of certain preparations of dextran of molecular weight (35–70) $\times 10^3$ and low degree of branching are effective substitutes for blood plasma. Hence, transport properties of aqueous solutions of dextrans should be of special interest to workers in various fields.

Dextran molecules in aqueous solutions have been studied using a number of experimental techniques: adiabatic compressibility [1,2], viscosity [2–4], light scattering [3,5], sedimentation velocity [3,4] and ultrasonic absorption coefficients [6]. In the present study, interdiffusion coefficients have been measured for seven well defined dextran fractions in aqueous solutions at 20, 25, 30 and fractions in aqueous solutions at 20, 25, 30 and 35°C. The results from these measurements will be discussed in the present communication.

2. Experimental procedure

2.1. Materials

A total of seven well defined dextran fractions (kindly donated by Dr. K. Granath, Pharmacia AB, Uppsala) were used in the present study. Gel permeation chromatography (GPC) analyses show that these fractions are sharp (table 1). Double-distilled water was used for all measurements.

2.2. Diffusion apparatus

The method used for measurements of the interdiffusion coefficients is that of free diffusion in which an initially sharp boundary is formed between a solution and the pure solvent. The diffusion measurements were performed in an apparatus designed at this Institute [7], using the boundary formation technique of Claesson et al. [8], and a modified Rayleigh interferometer to monitor the

0301-4622/82/0000–0000/$02.75

refractive index variation in the measuring cell [9]. The apparatus is situated in a thermally insulated room [7] and hence measurements at room temperature can be performed without a thermostat. At temperatures remote from the ambient one, a thermostating 'cap' was placed over the cell. Since an He-Ne laser (Spectra-Physics model 132) was used as the light source in the experimental arrangement, only red light ($\lambda = 633$ nm) was available and this limited the choice of high-contrast photographic material to be used for the registration of the interference patterns.

Ilford (R.20 Special Rapid, Panchromatic Backed) photographic plates have been used in the present investigations. By developing these plates in a hard developer, it was possible to obtain sufficient contrast for accurate measurements of the interference patterns on a microcomparator. A detailed description of the diffusion apparatus and technique of measurement is given elsewhere [10].

2.3. Diffusion measurements

Diffusion measurements were made on aqueous solutions of the dextrans at a temperature of 22–23°C, which did not vary by more than 0.4°C during each experiment. Measurements were carried out for each fraction at a series of concentrations, thus allowing the evaluation of the interdiffusion coefficients at infinite dilution. The interdiffusion coefficients at infinite dilution were corrected to the standard temperature of 25°C. Interdiffusion coefficients were also measured for the dextran fractions at 20, 30 and 35°C. Since the measurements at 25°C showed the interdiffusion coefficients to be independent of concentration, solute concentrations of approx. 1% by weight were used for all measurements at the other temperatures. For these later measurements, a thermostat was used. The constancy of the thermostat was within ± 0.1°C during all measurements.

2.4. Calculation of the diffusion coefficients from Rayleigh interferograms

The measurements of the photographic plates have been made on a high-precision microcomparator which was designed and built at this Institute [9].

Since a detailed description of the method used to obtain the diffusion coefficients from the Rayleigh interferograms has already been reported [11], only a brief outline will be given here.

The fringe function, j, is defined as the optical path difference, expressed as number of fringes, between a point in the cell during measurement and the same point when the cell is filled with pure solvent [9,11]. If the difference in the value of the fringe functions for two points symmetrically paired around the position of the original boundary in a diffusion process is denoted by δj and the corresponding difference in x-coordinates for these two points is δx, then δx is related to δj through the following expression [11]

$$(\delta x)^2 = \frac{4\pi\left(\frac{\delta j}{\Delta j}\right)^2}{\left[1 - \frac{\pi}{12}\left(\frac{\delta j}{\Delta j}\right)^2\right]^2} \cdot D^* \cdot t \qquad (1)$$

where Δj is the total change in fringe function across the boundary, D^* the diffusion coefficient corresponding to a given fringe pair, and t the time after the formation of the boundary.

Eq. 1 reduces to:

$$(\delta x)^2 = KD^* \cdot t \qquad (2)$$

where the coefficient K is defined by:

$$K = \frac{4\pi\left(\frac{\delta j}{\Delta j}\right)^2}{\left[1 - \frac{\pi}{12}\left(\frac{\delta j}{\Delta j}\right)^2\right]^2}$$

According to eq. 2, a plot of $(\delta x)^2$ for a given fringe pair vs. t should give a straight line with slope equal to KD^*. Since K is known through values of δj and Δj, D^* can be calculated.

The straight line resulting from the corresponding plots of D^* vs. $(\delta j)^2$ gives as the intercept D_A (the 'height – area' diffusion coefficient) for the solute concentration in question. From the plots of D_A vs. concentration C, the value of D_A at infinite dilution (D_0) is obtained. D_0 is then the so-called reduced height – area diffusion coefficient.

3. Results and discussion

3.1. Molecular weight dependence of D_0

Table 1 contains the experimentally determined values of the interdiffusion coefficients (D_0) at the various temperatures. The dependence of D_0 on the GPC average molecular weights $\overline{M}_w$ and $\overline{M}_n$ are given by the following relations of the form. $D_0 = KM^{-a}$

$$t = 20°C \begin{cases} D_0 = 11.0 \times 10^{-5} \overline{M}_w^{-0.51} \\ D_0 = 26.4 \times 10^{-5} \overline{M}_n^{-0.60} \end{cases}$$

$$t = 25°C \begin{cases} D_0 = 5.51 \times 10^{-5} \overline{M}_w^{-0.43} \\ D_0 = 11.5 \times 10^{-5} \overline{M}_n^{-0.51} \end{cases}$$

$$t = 30°C \begin{cases} D_0 = 8.00 \times 10^{-5} \overline{M}_w^{-0.46} \\ D_0 = 17.5 \times 10^{-5} \overline{M}_n^{-0.54} \end{cases}$$

$$t = 35°C \begin{cases} D_0 = 5.82 \times 10^{-5} \overline{M}_w^{-0.42} \\ D_0 = 11.9 \times 10^{-5} \overline{M}_n^{-0.49} \end{cases}$$

The values of the exponent a in the above equations exhibit an irregular variation with temperature. The highest values are, however, obtained at 20°C while the lowest values correspond to the highest temperature, 35°C. The irregular variations of a may be due to effects of hydration and branching of the dextran molecules. Hydration of dextran in dilute aqueous solution has been studied using the proton magnetic relaxation method [12]. The degree of hydration was found to increase with increasing molecular weight of the dextrans.

Data from intrinsic viscosity measurements on the dextran fractions at 25°C gave the following Mark-Houwink-Sakurada equations:

$$[\eta] = 1.58 \times 10^{-3} \overline{M}_w^{0.46}$$

$$[\eta] = 0.732 \times 10^{-3} \overline{M}_n^{0.54}$$

An unbranched [13] dextran should have an exponent b of about 0.68 in the equation. $[\eta] = KM^b$. The values of b in the above equations would then indicate that the dextrans used in the present investigation contain some branches, since b has been shown [4] to decrease with increasing degree of branching of dextran.

3.2. Temperature dependence of D_0

The dependence of D_0 on temperature is given by the following Arrhenius-type equation:

$$D_0 = D_\infty \exp\left(-\frac{E_D}{RT}\right) \tag{3}$$

where E_D is the activation energy of diffusion, D_∞ a constant ('the interdiffusion coefficient at an infinitely high temperature'), R the gas constant and T the absolute temperature. The plots of log D_0 vs. $1/T$ for the dextrans are shown in fig. 1. The data for the dextran fraction with $\overline{M}_n = 85\,000$ are not included in fig. 1 due to considerable overlapping of the experimental points. It is evident from fig. 1 that there is an appreciable scatter of the experimental points with increasing molecular weight and also polydispersity (table 1) of the

Table 1

Experimental data for the diffusion of the dextrans in aqueous solution

Fraction	$\overline{M}_w$ ($\times 10^{-4}$)	$\overline{M}_n$ ($\times 10^{-4}$)	$\frac{\overline{M}_w}{\overline{M}_n}$	D_0 ($cm^2\ s^{-1}$) ($\times 10^7$)				E_D (kcal mol^{-1})
				$t = 20°C$	$t = 25°C$	$t = 30°C$	$t = 35°C$	
1	2.15	2.05	1.05	6.54	7.31	8.23	9.38	4.31
2	2.56	2.42	1.06	6.04	6.84	7.47	8.56	4.07
3	3.24	3.01	1.08	5.27	6.11	6.96	7.42	4.17
4	5.33	4.81	1.11	4.04	4.85	5.19	6.13	4.74
5	9.58	7.20	1.33	3.10	3.76	4.01	4.94	5.25
6	11.20	8.50	1.32	2.77	3.56	3.88	4.66	5.93
7	13.20	9.90	1.33	2.58	3.40	3.62	4.27	6.02

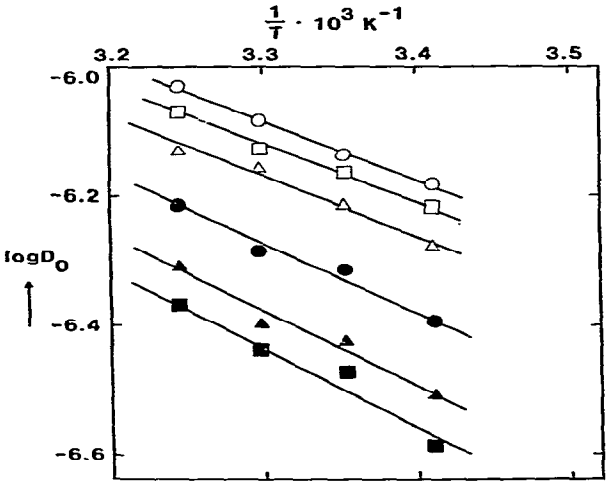

Fig. 1. Arrhenius plots of diffusion data for the dextran fractions in aqueous solutions: $\overline{M}_n = 20500$, ○; $\overline{M}_n = 24200$, □; $\overline{M}_n = 30100$, △; $\overline{M}_n = 48100$, ●; $\overline{M}_n = 72000$, ▲; $\overline{M}_n = 99000$, ■.

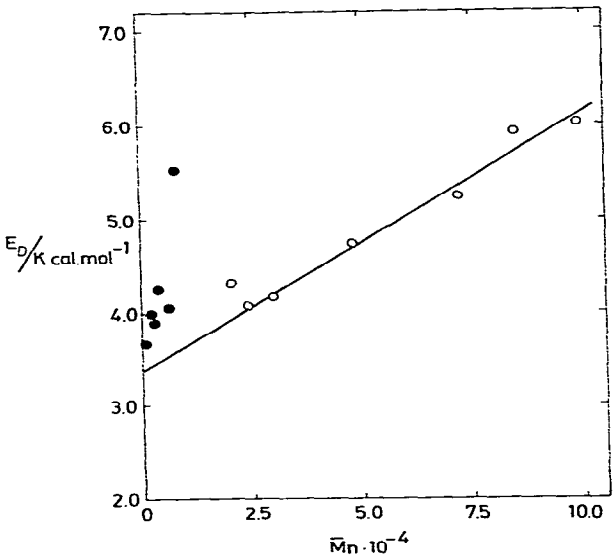

Fig. 2. Plot of activation energies (E_D) of diffusion for dextrans in aqueous solutions against the number average molecular weight ($\overline{M}_n$) of the dextran fractions: ○, data from present work; ●, from ref. 10.

dextran samples. The activation energies (E_D) for the dextrans have been calculated using the slopes obtained from plots of log D_0 vs. $1/T$ by the method of least squares, and eq. 3. The calculated E_D values are contained in the last column of table 1. The data are plotted in fig. 2 as E_D vs. the number average molecular weight ($\overline{M}_n$). Also included in fig. 2 are E_D values for some oligodextrans, from a separate study [10]. Fig. 2 shows that the variation of E_D with $\overline{M}_n$ is irregular up to about $\overline{M}_n = 20000$. For $\overline{M}_n > 20000$, E_D becomes an increasing function of $\overline{M}_n$ and this dependence is approximately linear. A linear fit of the experimental points corresponding to dextrans with $\overline{M}_n > 20000$ gives the following relation for the dependence of E_D on $\overline{M}_n$:

$$E_D = 2.763 \times 10^{-5}\, \overline{M}_n + 3.38 \quad (4)$$

Similarly, for the weight average molecular weight ($\overline{M}_w$):

$$E_D = 1.889 \times 10^{-5}\, \overline{M}_w + 3.61 \quad (5)$$

Selected literature values of E_D for self-diffusion of water are: 4.0 kcal mol^{-1} (25–65°C) [14]; 4.8 kcal mol^{-1} (5–25°C) [15]; 4.7 kcal mol^{-1} (1–15°C) [16]; 4.2 kcal mol^{-1} (15–45°C) [16]. The extrapolated E_D values for self-diffusion of water (3.38 and 3.61 kcal mol^{-1}) are of the right order of magnitude when compared to literature values.

Acknowledgements

The author cordially wishes to thank Dr. K. Granath, Pharmacia AB, Uppsala, for donating the dextran fractions used in the present study. He is also indebted to the Swedish Natural Science Research Council for financial support.

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