Study of aqueous dextran solutions under high pressures and different temperatures by dynamic light scattering

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The behaviour of dextrans of different molar masses in aqueous solutions was investigated by dynamic light scattering at different temperatures, ranging from 30 to 100°C and different pressures, in the range 1–3000 bar. It has been shown that concentration dependence of the apparent diffusion coefficient, D_{app}, of all samples changes the behaviour about the overlap concentration C^*. It has also been shown, that the diffusion coefficient increases with temperature (as a consequence of faster fluctuations of the molecules) and decreases with pressure. This could be accounted for by increase of solvent (water) viscosity with pressure. The activation energy of diffusion is independent of molar mass of dextran for the samples of molar masses from 7.4–$21.1 \times 10^6\ \text{g mol}^{-1}$, but it is considerably lower for the sample of molar mass of $1.0 \times 10^6\ \text{g mol}^{-1}$. Pressure has a very small effect on activation energy of diffusion. The characteristic exponent for diffusion coefficient D^0 dependence on molar mass was found to be 0.32.

(Keywords: dextran solutions; diffusion coefficient; dynamic light scattering)

INTRODUCTION

Dextrans are polysaccharides consisting essentially of α-1.6-linked D-glucose units. They differ in some structural details. They show a varying degree of branching at the 2-, 3- and/or 4-positions in the glucose residues. It has been shown, that the degree of branching increases with increasing molar mass[1].

Dextrans are produced by different strains of *Leuconostoc mesenteroides* and by other bacteria. Molar masses of dextrans as synthesized by these bacteria are several tens of millions. Dextrans of desired molar masses are produced by hydrolysis in dilute acid[2]. Dextrans are of great scientific, practical and technological interest. They are mainly used for medical applications such as blood plasma volume expanders and blood flow improvers, as well as for cosmetic applications and for various chemical applications.

The behaviour of aqueous dextran solutions is not completely understood. One of the major problems is that the solution properties change with time. Namely, if solutions of clinical-type dextrans are stored for prolonged periods of time, partial precipitation takes place. The aim of this paper is to study some thermodynamic properties of water solutions of dextrans under different conditions in order to enhance our understanding of behaviour of dextrans in water. Among others, the solution properties at the point of transition from dilute to semi-dilute regime are also of some interest. The solution properties at higher concentrations were found to be significantly different from those in the dilute regime. Cloizeaux[3] and later de Gennes[4] introduced a concept by which a semi-dilute solution is supposed to be separated rather sharply from the regime of dilute solution. The point of crossover is determined by the coil overlap concentration C^*. There are, however, different alternatives for defining C^*. According to Simha[5], for hexagonally packed spheres of macromolecules, one obtains:

$$C_S^* = 1.08/[\eta] \tag{1}$$

where $[\eta]$ is the limiting viscosity number of a polymer. According to Graessley[6], C^* would roughly correspond to the concentration at which the average chain spacing is $2S(0)$, $S(0)$ being the radius of gyration at zero concentration. With $S^2 = R^2/6$ (R^2 being the mean square end-to-end distance) and well known Fox–Flory equation[7]:

$$[\eta] = \Phi \frac{R^3(0)}{M_w} \tag{2}$$

One obtains:

$$C_G^* = 0.77/[\eta] \tag{3}$$

If concentrations are sufficiently larger than C^*, a transient network of entangled chains is assumed, and consequently all measurable quantities must become independent of the chain length of the individual molecules.

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Table 1 M_w, $[\eta]$, C_G^* and C_S^* of studied dextran samples

Code	$M_w \times 10^{-6}$ (g mol^{-1})	$[\eta]$ at 25°C (cm^3 g^{-1})	$C_G^* \times 10^3$ (g cm^{-3})	$C_S^* \times 10^3$ (g cm^{-3})
1	1.0	68.0	11.3	15.9
2	7.4	85.0	9.1	12.7
3	17.5	104.0	7.4	10.4
4	21.1	135.0	5.7	8.0

Polystyrene has been the most extensively studied polymer in this respect (ref. 8 and references therein). Here, we present some results concerning transition from dilute to semidilute behaviour in aqueous dextran solutions.

EXPERIMENTAL

The dextran samples for this study were obtained by acidic hydrolysis of native dextran prepared bacteriologically by *Leuconostoc mesenteroides* at the Zdravlje pharmaceutical works (Leskovac, Jugoslavia)[2]. The mass-average molar masses of the dextran fractions were determined by light scattering and are given in *Table 1* together with the limiting viscosity numbers, $[\eta]$ and characteristic concentrations according to Graessley[6], C_G^* and according to Simha[5], C_S^*.

Solutions of dextran in bidistilled water were prepared in appropriate vessels with shaking at 100°C for about 4 h. Dynamic light scattering measurements at various pressures and temperatures were carried out in a specially designed apparatus. Detailed information is given elsewhere[9,10]. The high pressure cell (Nova Swiss, Switzerland) allowed measurements at temperatures up to 150°C and pressures up to 4000 bar. An air-cooled argon-ion laser 162 (Spectra-Physics, USA) was used as a light source with a wavelength of 488 nm.

Light scattering fluctuations were detected at $\Theta = 90°$ by a photomultiplier tube 9863/100 KB (EMI, UK). The output signal was correlated by a correlator ALV-3000 (ALV, Germany) and then analysed by a Peacock computer.

Evaluation of the data was done by expanding the experimentally measured normalized autocorrelation function $g_1(t)$ in a series[11,12]:

$$g_1(t) = \exp(-q^2 D_{\text{app}} t)(1 + \mu_2 t^2/2! - \mu_3 t^3/3! + \ldots \quad (4)$$

with the scattering vector $q = (4\pi/\lambda)\sin\theta/2$, apparent translational diffusion coefficient, D_{app}, and moments μ_i, which are related to the molar mass distribution of the polymer.

RESULTS AND DISCUSSION

The typical semi-log plot of the correlation function for dextran in water is shown in *Figure 1*. The behaviour of dextran samples was studied at different concentrations at 30, 70 and 100°C, for samples 1 and 2, and 30, 50, 70 and 100°C for samples 3 and 4. At each temperature, the measurements were performed at pressures of 1, 500, 1000, 1500 and 2000 bar, for samples 1, 2 and 4, while for sample 3 measurements were done at 1, 1000, 2000 and 3000 bar.

In *Figures 2, 3, 4* and *5* the concentration dependences of D_{app} for samples 1, 2, 3 and 4, respectively, are shown at the temperatures and pressures indicated (for the sake of clarity D_{app}–C curves are shown only for the pressures of 1 and 2000 bar). Concentrations are exact and were calculated taking into account change in density of water with P and T.

From *Figures 2* and *3* it can be seen that for dextran samples 1 and 2, k_D values in equation[13]:

$$D_{\text{app}} = D^0(1 + k_D C + \cdots) \quad (5)$$

change from positive to negative, the change being observed in the range of concentrations C_G^* to C_S^*.

Curves in *Figures 4* and *5* were fitted by using second order linear regression. Careful examination of these curves shows that, for the samples 3 and 4, in the range of concentrations C_G^* to C_S^*, D_{app}–c functions deviate from straight line, seen at higher concentrations, to higher order behaviour at lower concentrations.

Translational diffusion coefficients at infinite dilution, D^0, were obtained by extrapolations according to

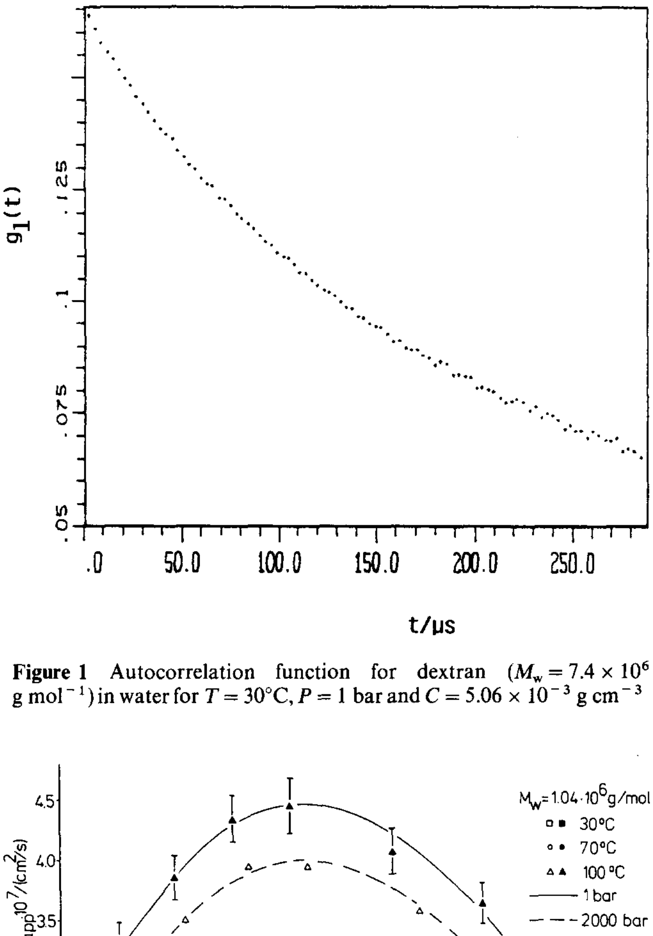

Figure 1 Autocorrelation function for dextran ($M_w = 7.4 \times 10^6$ g mol^{-1}) in water for $T = 30$°C, $P = 1$ bar and $C = 5.06 \times 10^{-3}$ g cm^{-3}

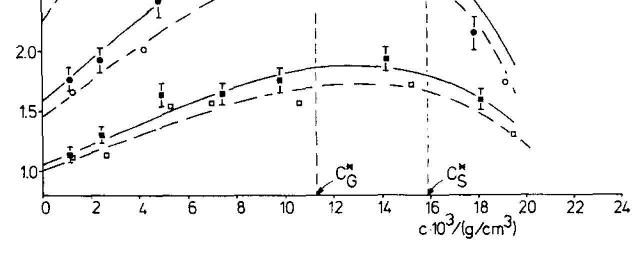

Figure 2 Concentration dependence of D_{app} in water for dextran 1 at various temperatures and pressures of 1 and 2000 bar

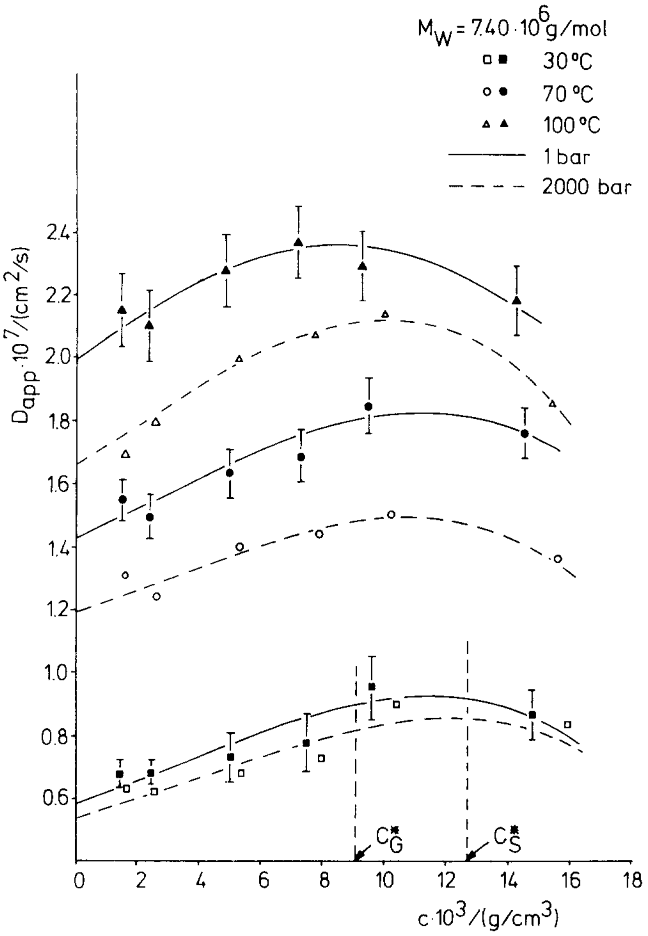

Figure 3 Concentration dependence of D_{app} in water for dextran 2 at various temperatures and pressures of 1 and 2000 bar

equation (5), for the samples 1 and 2, and by second order linear regression for samples 3 and 4. The values of D^0 for all samples increase with temperature at fixed pressure and decrease with pressure at constant temperature. In *Figure 6* D^0 values are presented as a function of T and P for the sample 3. Increase of D^0 with temperature at fixed pressure is in agreement with theoretical predictions[10] which indicate that this is a consequence of faster fluctuations of the macromolecules at higher temperature.

Decrease of D^0 with pressure at constant temperature is more pronounced at higher temperatures. The decrease of D^0 with increasing pressure at certain temperature can be accounted for by decrease of the volume with pressure, i.e., decrease of the number of holes available for the fluctuations of the molecules (expressed in terms of the lattice gas theory). This contribution can be subdivided in two parts: decrease of the number of holes leads to decrease of fluctuations of the dextran macromolecules; and decrease of the number of holes leads to decrease of fluctuations of the solvent molecules, leading to increase of solvent viscosity which directly influences the diffusion coefficient according to the Stokes–Einstein relation:

$$D^0 = kT/6\pi\eta R_h \tag{6}$$

where k is Boltzmann's constant, T is the absolute temperature and η is the solvent viscosity. The decrease of D^0 can also be accounted for by the influence of pressure on thermodynamic properties of the dextran solution.

The diffusion coefficient at finite concentration is determined by both thermodynamic and hydrodynamic interactions. Consequently, k_D (equation 5) is related to the second virial coefficient (A_2) and the concentration coefficient (k_f) in the concentration-dependence of the friction coefficient by the relationship[14]:

$$k_D + k_f = 2A_2M_w - v_2^{sp} \tag{7}$$

with

$$f(c) = f_0(1 + k_fc) \tag{8}$$

v_2^{sp} is the partial specific volume of the polymer and f_0 is related to D^0 via the Einstein relationship $D^0 = kT/f_0$.

Various theories of the concentration coefficient[15,16] k_f indicate that:

$$k_f = k_{f_0}(N_AV_h/M_w) \tag{9}$$

where N_A is Avogadros constant, V_h is the hydrodynamic volume of a molecule of molar mass M_w and k_{f_0} is a constant which characterizes the extent of coil interpenetration. Pyun and Fixman[16] have used an equivalent sphere, uniform segment density model to derive values of $k_{f_0} = 2.23$ for maximum interpenetration of solute molecules (the Θ-state for high molar mass polymers) and $k_{f_0} = 7.16$ for hard spheres (the 'good' solvent condition for high molar mass polymers).

By using equation (7) one can calculate A_2. In our calculation we neglect v_2^{sp} because it is small in comparison with the other two terms in equation (7). For k_{f_0}

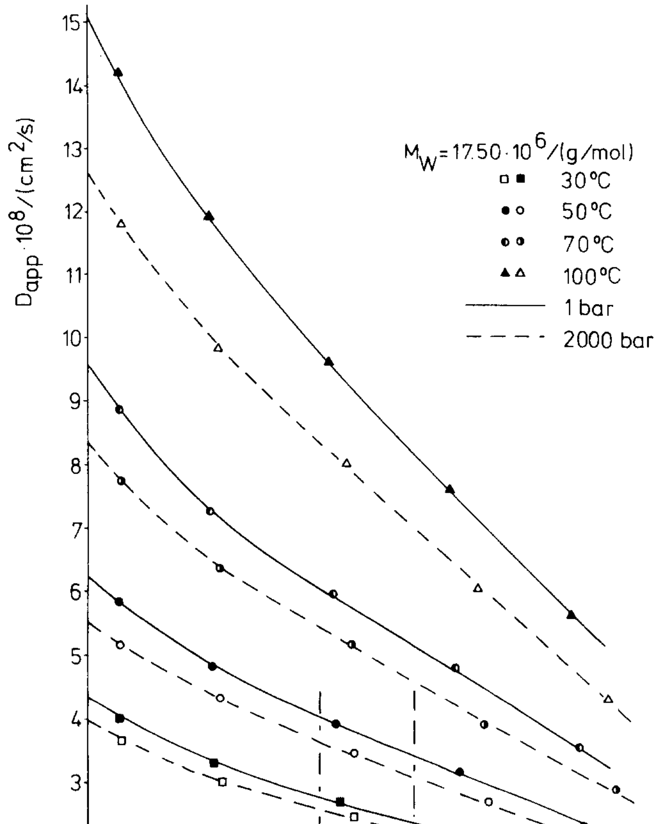

Figure 4 Concentration dependence of D_{app} in water for dextran 3 at various temperatures and pressures of 1 and 2000 bar

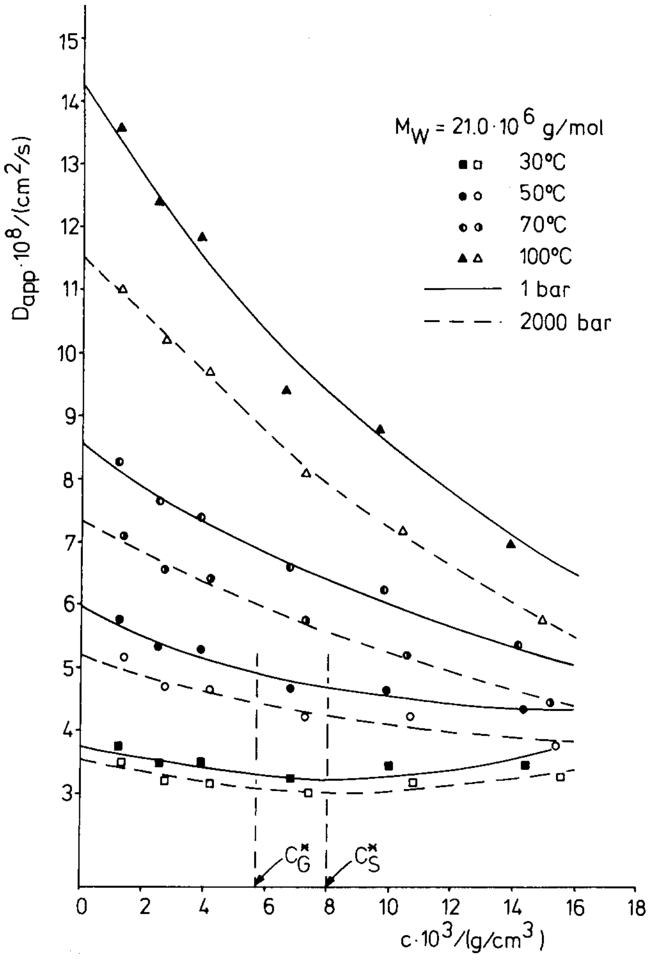

Figure 5 Concentration dependence of D_{app} in water for dextran 4 at various temperatures and pressures of 1 and 2000 bar

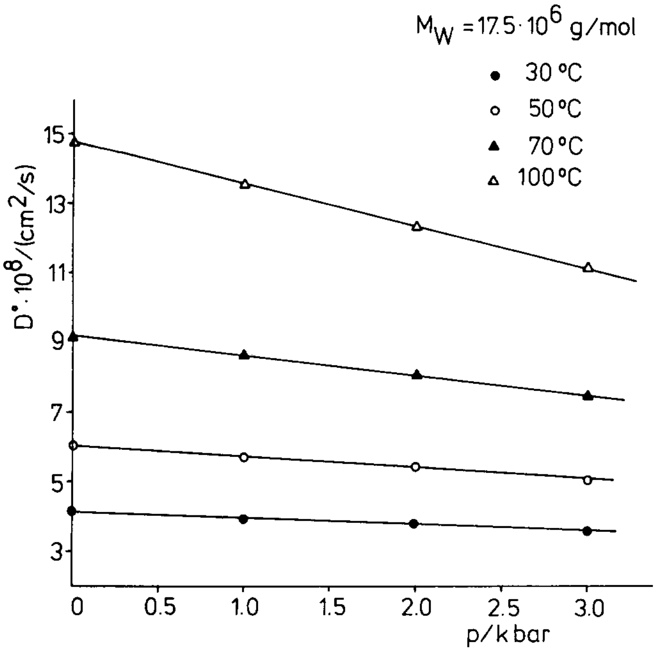

Figure 6 D^0 as a function of pressure for dextran in water at various temperatures

we chose the value of 2.23, but it is not of real consequence in our further treatment because we are only interested in influence of pressure on k_D and A_2.

In *Table 2* the values of D^0, R_h, k_D and A_2 for the dextran samples studied are presented at different temperatures and pressures of 1 and 2000 bar. It can be seen from *Table 2* that for all dextran samples both A_2 and R_h are, within experimental error, independent of pressure. The only exception may be sample 1 at temperatures of 30 and 70°C, where the change in A_2 with pressure exceeds somewhat the limits of the error.

In *Table 3* the ratios D^0_P/D^0_1 of sample 4 and η_1/η_P of water at different pressures and temperatures are shown (here the subscripts 1 and P indicate atmospheric and the considered pressure, respectively). Values of η for water at different pressures and temperatures were taken from data in ref. 17. From the data in *Tables 2* and *3* we may reasonably conclude that the pressure dependence of the dextran diffusion coefficient at infinite dilution is entirely correlatable to the change in solvent viscosity with pressure. Consequently, the pressure dependence of D^0 for this system may be expressed as:

$$D^0_P = D^0_1(\eta_1/\eta_P) \qquad (10)$$

The activation energy of diffusion, E_D, of dextran macromolecules was calculated from the equation:

$$D^0 = D_0 \exp(-E_D/RT) \qquad (11)$$

The data are collected in *Table 4*.

It can be seen from *Table 4* that E_D is independent of molar mass of dextran for the samples of higher molar masses. However, the E_D of the sample of lowest molar mass is dramatically lower than for the other three samples. It is probably the consequence of branching in dextran macromolecules, because it is known, that branching is increasing with the molar mass of dextran[18] and in that respect sample 1 is the least branched. The effect of pressure on E_D is very small.

The molar mass dependence of D^0 is shown in *Figure 7* for 30°C and $P = 1$ bar. The relationship between D^0 and molar mass can well be represented by relation:

$$D^0 = k_T M_w^{-b} \qquad (12)$$

The temperature dependent factor k_T was calculated as 9.44×10^{-6} m^2 s^{-1}, while the exponent b is 0.32 and is lower than that theoretically calculated ($b = 0.600$) or experimentally found for dextran of lower molar masses

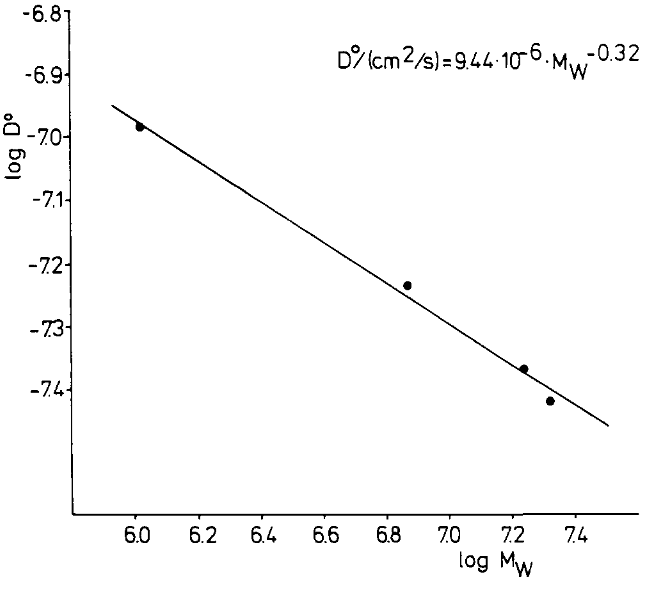

Figure 7 Dependence of D^0 on molar mass of dextran in water at 30°C and a pressure of 1 bar

Table 2 D^0, R_h, k_D and A_2 for studied samples of dextran at different temperatures and pressures

Sample code	T (°C)	P (bar)	$D^0 \times 10^8$ (cm^2 s^{-1})	R_h (nm)	k_D (cm^3 g^{-1})	A_2 (cm^3 mol g^{-2})
1	30	1	10.4	26.7	81.5	8.5×10^{-5}
		2000	10.0	24.7	71.4	7.4×10^{-5}
	70	1	15.8	38.8	124.1	2.1×10^{-4}
		2000	14.6	35.5	100.7	1.6×10^{-4}
	100	1	26.0	37.0	105.8	1.8×10^{-4}
		2000	22.6	34.6	112.4	1.6×10^{-4}
2	30	1	5.8	47.8	63.3	9.9×10^{-6}
		2000	5.3	46.5	59.2	9.2×10^{-6}
	70	1	14.2	43.2	32.9	6.4×10^{-6}
		2000	11.9	43.5	29.0	6.2×10^{-6}
	100	1	20.0	48.1	30.8	7.8×10^{-6}
		2000	16.6	47.0	35.5	7.7×10^{-6}
3	30	1	4.2	66.5	−49.6	1.3×10^{-6}
		2000	3.8	65.3	−45.2	1.3×10^{-6}
	50	1	6.1	71.1	−51.0	1.8×10^{-6}
		2000	5.4	70.1	−46.3	1.9×10^{-6}
	70	1	9.2	67.0	−48.4	1.4×10^{-6}
		2000	8.0	64.5	−47.4	1.1×10^{-6}
	100	1	14.8	65.2	−49.3	1.1×10^{-6}
		2000	12.3	63.4	−47.1	1.0×10^{-6}
4	30	1	9.8	72.8	−29.4	1.7×10^{-6}
		2000	3.5	69.7	−31.6	1.4×10^{-6}
	50	1	8.5	71.8	−37.9	1.5×10^{-6}
		2000	7.3	70.7	−33.4	1.5×10^{-6}
	70	1	6.0	72.2	−38.2	1.5×10^{-6}
		2000	5.2	72.8	−28.1	1.8×10^{-6}
	100	1	14.5	66.3	−53.7	4.5×10^{-7}
		2000	11.5	67.8	−54.0	4.6×10^{-7}

Table 3 D_p^0/D_1^0 for dextran sample 4 and η_1/η_p of water at different temperatures and pressures

T (°C)	P (*bar*)	D_p^0/D_1^0	η_1/η_p
30	1	1.00	1.000
	500	1.00	0.976
	1000	0.97	0.953
	1500	0.95	0.920
	2000	0.93	0.890
50	1	1.00	1.000
	500	0.97	0.976
	1000	0.92	0.946
	1500	0.92	0.911
	2000	0.97	0.878
70	1	1.00	1.000
	500	0.96	0.969
	1000	0.93	0.932
	1500	0.90	0.882
	2000	0.86	0.845
100	1	1.00	1.000
	500	0.94	0.947
	1000	0.90	0.910
	1500	0.88	0.861
	2000	0.79	0.811

Table 4 The activation energy of diffusion, E_D, for the dextran studied at pressures of 1 and 2000 bar

$M_w \times 10^{-6}$ (g mol^{-1})	P (bar)	E_D (kJ mol^{-1})
1.04	1	11.5
	1000	10.2
7.40	1	17.6
	2000	16.3
17.50	1	17.1
	2000	16.0
21.05	1	17.7
	2000	16.8

($b = 0.552$) (ref. 18), but in agreement with our previous results[19]. The obvious discrepancy can probably be explained by a higher degree of branching of the dextran samples used in our work.

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