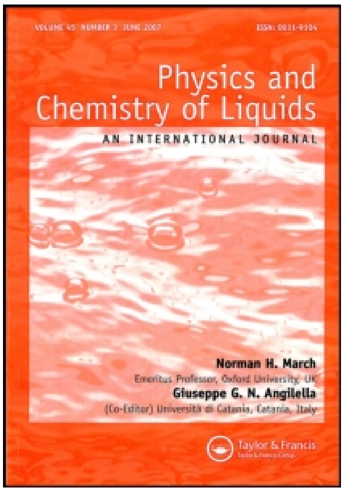

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THE VISCOSITY OF DILUTE SOLUTION OF A NOVEL POLYMER 'DEXTRAN' IN DIFFERENT SOLVENTS

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The viscosity of dilute solution of a water soluble polysaccharide "Dextran" has been studied in 6(M) Urea, 2(M) Glycine and 50% Glucose solution in three different temperatures - 40°C, 45°C and 50°C. From the solution viscosity measurement, thermo viscosity parameters like Huggins' constant (k'_H). Kraemer's constant (k''_H) and the viscosity concentration coefficient (a_2) have been estimated from viscosity concentration plots. The value of these parameters have been characterized and compared with the theoretical value. The evaluation of these constants enable to know the fate of polymer molecules in the solution.

Keywords: Polymer 'Dextran'; Huggins' constant; Kraemer's constant; viscosity concentration coefficient

INTRODUCTION

Investigation on the solution structures [1] of polymer have been carried out in recent past by various researchers [2-4] from different angles [5]. Earlier we [6] have studied the molecular interaction of a novel polymer "Dextran" of molecular weight 75000 and 250000 in solvents *viz.* Distilled water, 1(N) NaOH and 1(N) KOH in different temperature range through evaluation of thermoviscosity parameters

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like Huggins constant, Kraemer's constant and viscosity concentration coefficient.

In continuation of this study we have made an investigation on molecular interaction of above mentioned polymer in new sets of solvents like 6(M) Urea, 2(M) Glycine and 50% Glucose and evaluated various thermo-viscosity parameters. A comparison of these parameters will throw light on the property of Dextran.

THEORY

The concentration dependence of the viscosity of dilute polymer solutions can be expressed in a power series in concentration.

$$\eta = \eta_0(1 + \mathrm{H_1c} + \mathrm{H_2c^2} + \mathrm{H_3c^3} + \cdots) \tag{1}$$

where 'η' and 'η_0' denote the viscosity of solution and solvent respectively.

The relative viscosity is defined as the ratio of viscosity of solution (η) to that of the solvent (η_0). The working formula for calculating relative viscosity is defined as the ratio of efflux time of solution (t) to that of solvent (t_0).

$$\eta_{\mathrm{rel}} = \eta/\eta_0 = t/t_0 \tag{2}$$

Equation (1) can be written in more familiar form

$$\eta - \eta_0/\eta_0 c = \eta_{\mathrm{sp}}/c = [\eta] + k_1[\eta]^2 c + k_2[\eta]^3 c^2 + \cdots \tag{3}$$

where specific viscosity is defined as $\eta_{\mathrm{sp}} = \eta_{\mathrm{rel}} - 1 = (\eta/\eta_0) - 1 = (t/t_0) - 1$ or,

$$\eta_{\mathrm{sp}} = (\eta - \eta_0)/\eta_0 = (t - t_0)/t_0 \tag{4}$$

$[\eta]$ is intrinsic viscosity and $k_i(k_1, k_2, \ldots.)$ of Eq. (3) are dimensionless parameters and k_1 corresponds to Huggins' coefficient k_H'

Intrinsic viscosity is defined as

$$[\eta] = \lim_{c \to 0}(\eta_{\mathrm{sp}}/c) \tag{5}$$

Intrinsic viscosity is independent of the concentration of the solution but is a function of the solvent used. It is obtained from the intercept of the plot (η_{sp}/c) *versus* concentration (c) graph at zero concentration.

For low concentration we obtained Huggins' [7] well known relationship

$$\eta_{sp}/c = [\eta] + k'_H[\eta]^2 c \tag{6}$$

where η_{sp}/c is known as reduced viscosity.

The equation given by Kraemer [8] is often used for extrapolation because of the small concentration dependence. This relationship is most conveniently written as

$$\ln(\eta_{rel})/c = [\eta] + k''_H[\eta]^2 c \tag{7}$$

where $\ln(\eta_{rel})/c$ is known as the inherent viscosity and k''_H is Kraemer's constant.

EXPERIMENT

Materials: Dextran ($\overline{M}_w = 75000$ and 250000) was a gift from Dextran Products Limited, Canada. A freshly prepared solution of (1 wt%) the sample was prepared in solvents like 6(M) Urea, 2(M) Glycine and 50% Glucose. The AA/solvents like Urea, Glycine and Glucose are BDH (AR) grade and used as such throughout the experiment.

Method: (Viscosity Measurement)

The viscosity measurement was carried out in an Ubbelohde type suspended level dilution viscometer. 6(M) Urea, 2(M) Glycine and 50% Glucose solution were prepared and their efflux time were measured in three different temperatures: – 40°C, 45°C and 50°C. 1% Dextran solutions were prepared in above mentioned solvents and their efflux times were measured in the above mentioned temperature range. Reducing the concentration of the polymer solution by adding an instalment of 2 ml. solvent solution, their efflux times were measured in the same temperature range. The relative viscosity (η_{rel}), and specific viscosity (η_{sp}) were calculated using Eqs. (2) and (4) respectively.

Graphs were plotted of reduced viscosity (η_{sp}/c) *versus* concentration (c) for all the three solvents at three different temperatures. Another graph was plotted between inherent viscosity $\ln(\eta_{\text{rel}})/c$ *versus* concentration (c). Extrapolating the graphs for concentration "$c = 0$", the intrinsic viscosity $[\eta]$, viscosity concentration coefficient 'a_2', Huggins' constant (k'_H) and Kraemer's constant (k''_H) were calculated for all three solvents.

RESULTS AND DISCUSSION

The flow time of the novel polymer Dextran ($\overline{M}_w = 75000$ and 250000) in solvents such as 6(M) Urea, 2(M) Glycine and 50% Glucose has been measured at three different temperatures: – 40°C, 45°C and 50°C and varying concentration. The flow times of these solvents and polymer solution were measured. These experimental data were then used to calculate the thermoviscosity parameters such as Huggins' constant, Kraemer's constant and viscosity concentration coefficient in these mixtures. These relative data are shown in Figures 1 to 6 and in the Tables I, II and III.

In aqueous solutions of the fractioned Dextran ($\overline{M}_w = 75000$ and 250000) plots of (η_{sp}/c) *versus* (c) and ($\ln \eta_{\text{rel}}/c$) *versus* (c) give straight lines as illustrated in Figures 1 to 6.

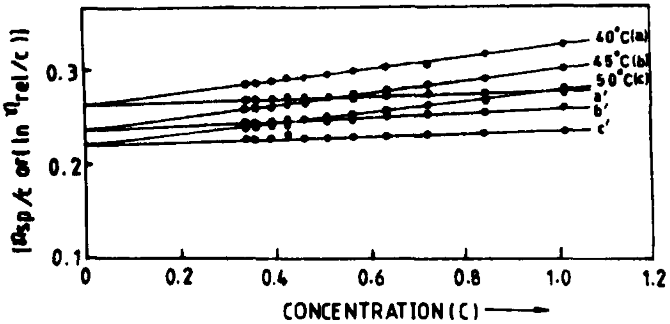

FIGURE 1 $\eta_{\text{sp}/c}$ (a, b, c) and $\ln \eta_{\text{rel}/c}$ (a', b', c') plotted against concentration (c) for fractionated Dextran ($\overline{M}_w = 75000$) in 6(M) Urea at different temperatures.

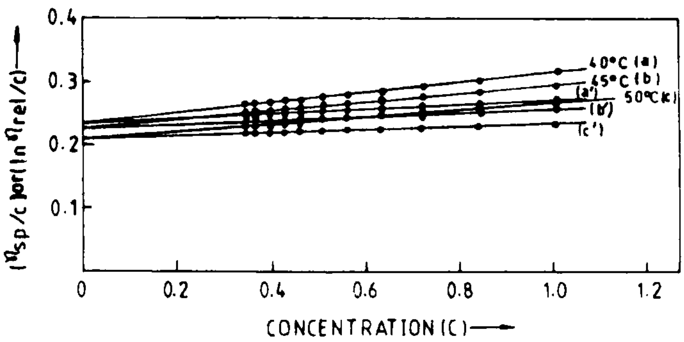

FIGURE 2 $\eta_{sp/c}$ (a, b, c) and $\ln \eta_{rel/c}$ (a', b', c') plotted against concentration (c) for fractionated Dextran ($\bar{M}_w = 75000$) in 2(M) Glycine at different temperatures.

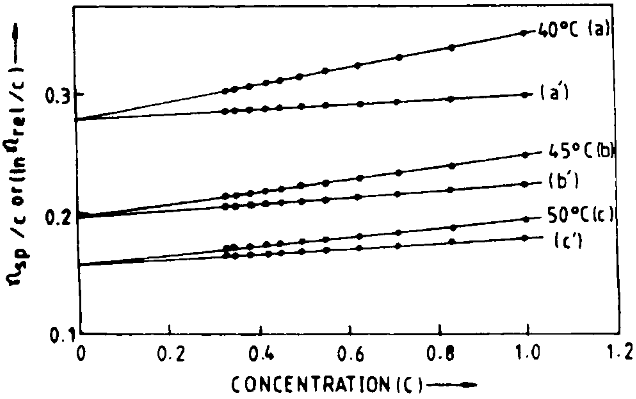

FIGURE 3 $\eta_{sp/c}$ (a, b, c) and $\ln \eta_{rel/c}$ (a', b', c') plotted against concentration (c) for fractionated Dextran ($\bar{M}_w = 75000$) in 50% Glucose at different temperatures.

The specific viscosity of the polymer may be generally expressed as

$$\eta_{sp} = a_1 c + a_2 c^2 + a_3 c^3 + \cdots$$

Considering the dilute solution, terms higher than the second degree are neglected which leads to $\eta_{sp}/c = a_1 + a_2 c$.

According to Huggins, $a_2 = k'_H[\eta]^2$, so that $\eta_{sp}/c = [\eta] + k'_H[\eta]^2 c$. Values of a_2 and k'_H, estimated from the viscosity measurement of aqueous Dextran in different solvents as well as at three different temperatures as shown in Tables I, II and III.

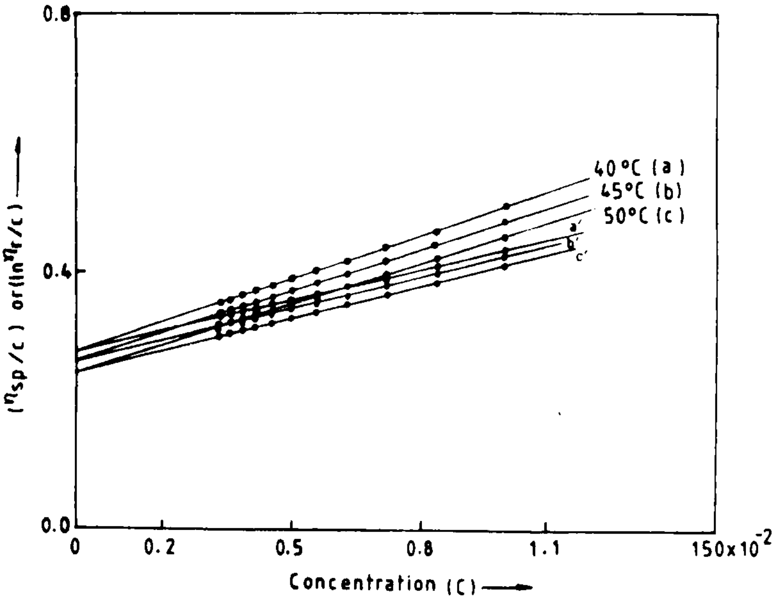

FIGURE 4 $\eta_{sp/c}$ (a, b, c) and $\ln \eta_{r/c}$ (a', b', c') plotted against concentration (c) for fractionated Dextran of $\overline{M}_w = 250000$ in 6(M) Urea at different temperatures.

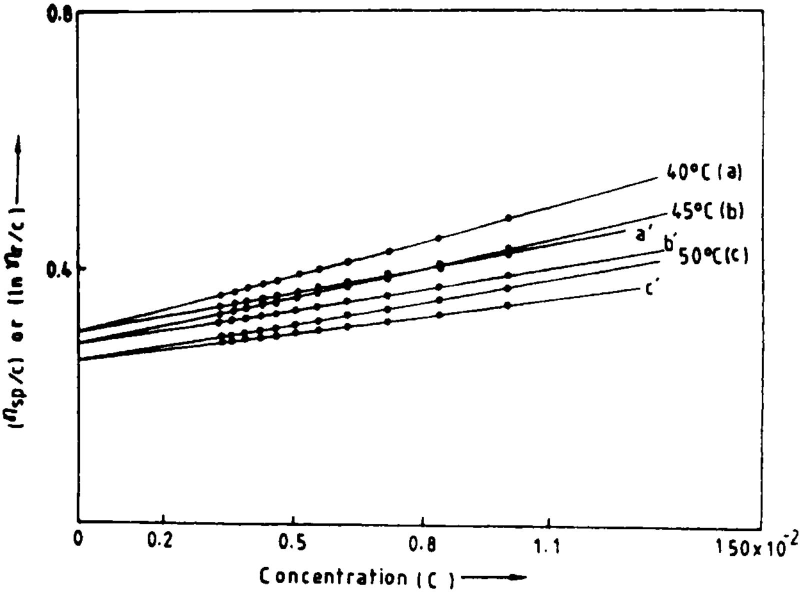

FIGURE 5 $\eta_{sp/c}$ (a, b, c) and $\ln \eta_{r/c}$ (a', b', c') plotted against concentration (c) for fractionated Dextran of $\overline{M}_w = 250000$ in 2(M) Glycine at different temperatures.

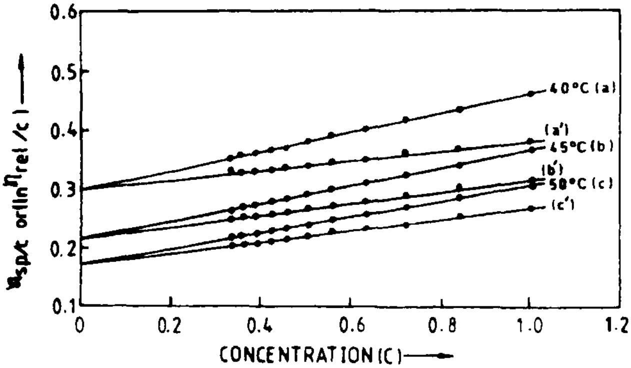

FIGURE 6 $\eta_{sp/c}$ (a, b, c) and $\ln \eta_{rel/c}$ (a', b', c') plotted against concentration (c) for fractionated Dextran $\overline{M}_w = 250000$ in 50% Glucose at different temperatures.

When (η_{sp}/c) *versus* (c) or $(\ln \eta_{rel}/c)$ *versus* (c) curve is extrapolated for infinite dilution $(c = 0)$ then the y-axis intercept gives the value of intrinsic viscosity $[\eta]$. It is observed that intrinsic viscosity of a given polymer solution decreases with rise in temperature which is in agreement with the theory that as temperature increases the intermolecular force of attraction decreases and hence viscosity decreases.

It is a point of interest and remarkable as to record that the intrinsic viscosity is more for Dextran of molecular weight 250000 in comparison to Dextran of molecular weight 75000. This is in good agreement with the theory that for higher molecular weight, the intermolecular force of attraction is more and hence viscosity is enhanced.

The calculated value of 'a_2' is given by the equation

$$a_2 = 0.201[\eta]^{2.28} \quad [9]$$

and is in good agreement with the experimental result obtained from the slope of (η_{sp}/c) *versus* (c) curve. However with rise in temperature there is a great deal of variation between theoretical and experimental value of 'a_2' which might be due to the fact that the temperature aspect had not been fully taken into consideration in deriving the equation.

The variation of viscosity with concentration as given by Eq. (6) is applicable for low concentration. Huggins well known relation (*i.e.*, Eq. (6)) is based upon Stoke's law. But Stoke's law can be applicable if each sub-molecule were isolated from all others, so that the liquid

TABLE I Intrinsic viscosity $[\eta]$, Huggins' constant (k'_H), Kraemer's constant (k''_H), viscosity concentration coefficient (a_2) of 1% Dextran in 6(M) Urea at 40°C, 45°C and 50°C for $\overline{M}_w$ = 75000 and 250000

Temp.	*Intrinsic viscosity* $[\eta]$		*Huggins' constant* k'_H		*Kraemer's constant* k''_H		$a_2 = k'_H[\eta]^2$ (*expt. value*)		$a_2 = .201\ [\eta]^{2.28}$ (*theo. value*)		$k'_H - k''_H$	
in °C	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$
40	0.270	0.273	0.837	2.930	0.343	2.460	0.061	0.220	0.070	0.072	0.494	0.470
45	0.243	0.259	1.008	2.880	0.491	2.460	0.059	0.193	0.055	0.064	0.517	0.420
50	0.228	0.242	0.962	2.746	0.385	2.136	0.050	0.162	0.048	0.055	0.577	0.610

TABLE II Intrinsic viscosity $[\eta]$, Huggins' constant (k'_H), Kraemer's constant (k''_H), viscosity concentration coefficient (a_2) of 1% Dextran in 2(M) Glycine at 40°C, 45°C and 50°C for $\overline{M}_w$ = 75000 and 250000

Temp.	*Intrinsic viscosity* $[\eta]$		*Huggins' constant* k'_H		*Kraemer's constant* k''_H		$a_2 = k'_H[\eta]^2$ (*expt. value*)		$a_2 = .201\ [\eta]^{2.28}$ (*theo. value*)		$k'_H - k''_H$	
in °C	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$
40	0.235	0.300	1.484	1.856	0.909	1.354	0.082	0.167	0.051	0.089	0.575	0.502
45	0.228	0.280	1.193	1.735	0.673	1.148	0.062	0.136	0.048	0.076	0.520	0.587
50	0.210	0.253	1.293	1.703	0.680	1.265	0.057	0.109	0.040	0.061	0.613	0.438

TABLE III Intrinsic viscosity $[\eta]$, Huggins' constant (k'_H), Kraemer's constant (k''_H), viscosity concentration coefficient (a_2) of 1% Dextran in 50% Glucose at 40°C, 45°C and 50°C for $\overline{M}_w = 75000$ and 250000

Temp. in °C	*Intrinsic viscosity* $[\eta]$		*Huggins' constant* k'_H		*Kraemer's constant* k''_H		$a_2 = k'_H[\eta]^2$ *(expt. value)*		$a_2 = .201\ [\eta]^{2.28}$ *(theo. value)*		$k'_H - k''_H$	
	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$	$\overline{M}_w = 75000$	$\overline{M}_w = 250000$
40	0.280	0.300	0.804	1.589	0.228	0.926	0.063	0.143	0.076	0.089	0.576	0.663
45	0.198	0.216	1.199	2.872	0.638	2.233	0.047	0.134	0.035	0.042	0.561	0.639
50	0.158	0.173	1.162	4.177	0.653	3.632	0.029	0.125	0.021	0.025	0.509	0.545

streaming past one would not be affected by the disturbances of the streaming around other sub molecules. The use of Eq. (6) involves the assumptions that the submolecules are spherical and are large relative to the solvent molecules. The objection to the use of Stoke's law in order to derive Huggins' equation can be met with the introduction of a fractor k' having a magnitude characteristic of the system under consideration – depending upon the size, shapes and cohesional properties of both solvent and solute molecules. The factor k_H' known as Huggins' coefficient can be calculated from (η_{sp}/c) *versus* (c) curve. According to the hydrodynamic theory of Riseman and Ullman the value of k_H' would be greater than one for spherical particles and our experimental value of k_H' is in fair agreement with the theoretical value.

The Kraemer's constant can be calculated from the $\ln(\eta_{rel}/c)$ *versus* concentration (c) curve. Comparing Eq. (7) with the experimental result we found that k_H'' is negative. It is of interest to record that $k_H' - k_H''$ is found to be nearly 0.5, whereas for linear flexible polymer system $k_H' + k_H''$ is 0.5 [10].

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