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## Physics and Chemistry of Liquids

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### Evaluation of Huggins' Constant, Kraemer's Constant and Viscosity Concentration Coefficient of Polymer Dextran in Urea, Glycine and Glucose

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# EVALUATION OF HUGGINS' CONSTANT, KRAEMER'S CONSTANT AND VISCOSITY CONCENTRATION COEFFICIENT OF POLYMER DEXTRAN IN UREA, GLYCINE AND GLUCOSE

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Reduced viscosity ( $\eta_{sp}/c$ ) and Inherent viscosity ( $\ln \eta_{rel}/c$ ) of dilute solution of water soluble polysaccharide polymer "Dextran" has been calculated by measuring the flow time of the polymer solution in solvents like 6(M) Urea, 2(M) Glycine and 50% Glucose at three different temperatures – 25°C, 30°C and 35°C. From extrapolation of curve ( $\eta_{sp}/c$ ) versus ( $c$ ) and ( $\ln \eta_{rel}/c$ ) versus ( $c$ ), thermo viscosity parameters like Huggins' constant ( $k'_H$ ), Kraemer's constant ( $k''_H$ ) and viscosity concentration coefficient ( $a_2$ ) have been estimated which enable us to know the fate of the polymer molecules in these solvents.

**Keywords:** Huggin's constant; Kraemer's constant; Intrinsic viscosity

## INTRODUCTION

Viscosity measurements of polymer solution provide an important measure about the existence of molecular interactions between the polymer and the solvents and the extent of interaction can also be predicted. Attempts in these directions have been made by number of researchers [1–6]. Earlier we [7, 8] have studied the molecular

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interaction of a novel polymer "Dextran" of molecular weight 75000 and 250000 in solvents like Distilled water, 1(N) NaOH, and 1(N) KOH at six different temperature ranging from 25°C to 50°C and also in solvents like 6(M) Urea, 2(M) Glycine and 50% Glucose at three different temperature 40°C, 45°C and 50°C.

In continuation of this study we have made an investigation on molecular interaction of polymer 'Dextran' in solvents like 6(M) Urea, 2(M) Glycine and 50% Glucose at three different temperatures – 25°C, 30°C and 35°C and evaluated various thermo-viscosity parameters which will throw light on the property of Dextran.

## THEORY

The rate of flow of polymer solution at any instant will be proportional to the pressure difference which is again proportional to the density ( $\rho$ ) and inversely proportional to the viscosity ( $\eta$ ) of the polymer solution. The volume of the polymer solution that will flow in time ' $t$ ' is given by

$$V = \int_0^t \frac{dv}{dt} dt = \int_0^t \frac{k\rho}{\eta} dt \quad (1)$$

or,  $V = \frac{k\rho t}{\eta}$

where 'k' is the constant for the viscometer, same volume ( $V$ ) of pure solvent of density ( $\rho_0$ ) and viscosity ( $\eta_0$ ) flowing in time ' $t_0$ ' is given by

$$V = \frac{k\rho_0 t_0}{\eta_0} \quad (2)$$

From Eqs. (1) and (2) we get,

$$\frac{\rho t}{\eta} = \frac{\rho_0 t_0}{\eta_0}$$

or  $\frac{\eta}{\eta_0} = \left(\frac{\rho}{\rho_0}\right) \left(\frac{t}{t_0}\right) \quad (3)$

where ( $\eta/\eta_0$ ) is known as the relative viscosity.

As we are considering very dilute polymer solution so the density of the polymer solution ( $\rho$ ) can be approximated to the density of the pure solvent ( $\rho_0$ ).

By taking this approximation Eq. (3) becomes

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0} \tag{4}$$

The concentration dependence [9–11] of the viscosity of dilute polymer solution can be expressed in a power series in concentration.

$$\eta = \eta_0(1 + H_1c + H_2c^2 + H_3c^3 + \dots) \tag{5}$$

This can be written in more familiar form as

$$\frac{\eta - \eta_0}{\eta_0c} = \frac{\eta_{sp}}{c} = [\eta] + k_1[\eta]^2c + k_2[\eta]^3c^2 + \dots \tag{6}$$

where specific viscosity is defined as

$$\begin{aligned} \eta_{sp} &= \eta_{rel} - 1 = \frac{\eta}{\eta_0} - 1 = \frac{t}{t_0} - 1 \\ \text{or } \eta_{sp} &= \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} \end{aligned} \tag{7}$$

$[\eta]$  is the intrinsic viscosity that is

$$[\eta] = \lim_{c \rightarrow 0} \left( \frac{\eta_{sp}}{c} \right) \tag{8}$$

and  $k_i(k_1, k_2, \dots)$  of Eq. (6) are dimensionless parameters and  $k_1$  corresponds to Huggins' constant ( $k'_H$ ).

Intrinsic viscosity is independent of concentration of the solution but is a function of the solvent used. For low concentration we obtained Huggins [12] well known relationship.

$$\frac{\eta_{sp}}{c} = [\eta] + k'_H[\eta]^2c \tag{9}$$

where  $(\eta_{sp}/c)$  is known as the reduced viscosity.

The equation given by Kraemer [13] is often used for extrapolation because of small concentration dependence. This relationship is most conveniently written as

$$\frac{\ln \eta_{\text{rel}}}{c} = [\eta] + k_H'' [\eta]^2 c \quad (10)$$

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

Finally, viscosity concentration coefficient [14] can be calculated by the equation:

$$a_2 = .201 [\eta]^{2.28} \quad (11)$$

## EXPERIMENT

### Requisites

- (i) **Polymer:** The polymer Dextran of molecular weight 75000 and 250000 which was obtained as a gift sample from Dextran products Limited, Canada and was used as such without any further purification.
- (ii) **Solvents:** Solvents used were Urea, Glycine and Glucose and these were BDH- Analar grade and used as such throughout the experiment.
- (iii) **Viscometer:** The solution viscosities of polymer solution as well as solvent were determined by a Viscometer. We used Ubbelohde Suspended Level Viscometer (USLV) for our study. It is a simple glass capillary device. It is designed in such a manner that the measurement is unaffected by the volume of the solution taken.

### Method (Viscometric Measurement)

The experimental determination of viscosity leading to the evaluation of Huggins' constant ( $k_H'$ ), Kraemer's constant ( $k_H''$ ) and viscosity concentration coefficient ( $a_2$ ) of polymer Dextran in Urea, Glycine and

Glucose at three different temperatures is the same as described in our earlier paper [8].

## RESULTS AND DISCUSSION

The flow ( $t$ ) of the polymer Dextran ( $\bar{M}_w = 75000$  and  $250000$ ) in solvent like 6(M) Urea, 2(M) Glycine and 50% Glucose had been measured at three different temperatures  $25^\circ\text{C}$ ,  $30^\circ\text{C}$  and  $35^\circ\text{C}$  and varying concentration. The flow times ( $t_0$ ) of the above mentioned pure solvents were measured at these temperatures. Using Eqs. (4) and (7) the relative viscosity ( $\eta_{\text{rel}}$ ) and specific viscosity ( $\eta_{\text{sp}}$ ) were calculated respectively. For different concentrations, reduced viscosity ( $\eta_{\text{sp}}/c$ ) and inherent viscosity ( $\ln \eta_{\text{rel}}/c$ ) were calculated.

Graphs were plotted between reduced viscosity ( $\eta_{\text{sp}}/c$ ) versus concentration ( $c$ ) for all the three solvents at three different temperatures. Another set of graphs were 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 ( $k'_H$ ) were calculated for all the three solvents.

The specific viscosity of the polymer generally expressed in terms of a power series in concentration as

$$\eta_{\text{sp}} = a_1c + a_2c^2 + a_3c^3 + \dots \quad (12)$$

considering a highly dilute solution, terms higher than the second degree of the above expression can be neglected, which leads to

$$\frac{\eta_{\text{sp}}}{c} = a_1 + a_2c \quad (13)$$

Comparing this with Huggins equation (Eq. (9)) we get

$$a_2 = k'_H[\eta]^2 \quad (14)$$

In aqueous solutions of the polymer Dextran ( $\bar{M}_w = 75000$  and  $250000$ ) the plot of ( $\eta_{\text{sp}}/c$ ) versus ( $c$ ) gives straight line as illustrated in Figures 1 to 6. These curves were extrapolated for infinite dilution

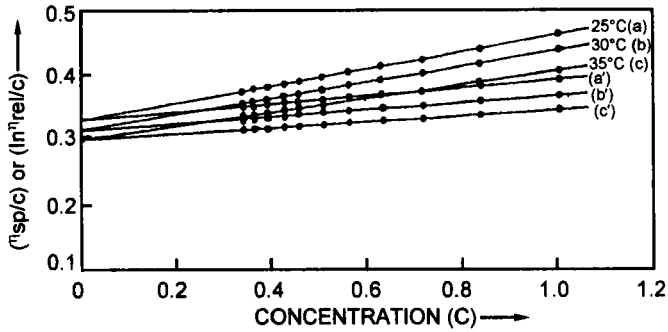


FIGURE 1  $\eta_{sp}/c(a, b, c)$  and  $\ln \eta_{rel}/c(a', b', c')$  plotted against concentration ( $c$ ) for Dextran ( $M_w = 75000$ ) in 6(M) Urea at different temperature.

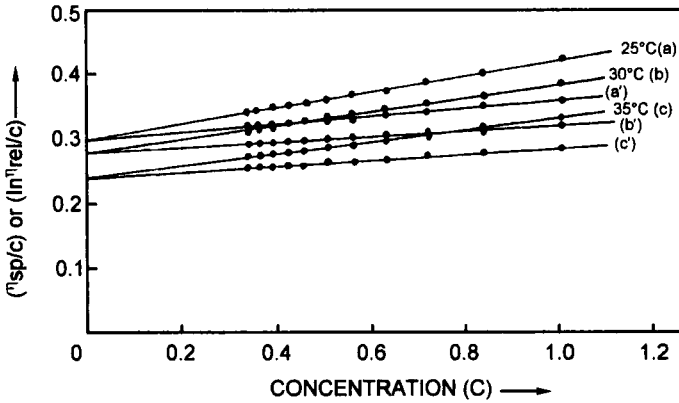


FIGURE 2  $\eta_{sp}/c(a, b, c)$  and  $\ln \eta_{rel}/c(a', b', c')$  plotted against concentration ( $c$ ) for Dextran ( $M_w = 75000$ ) in 2(M) Glycine at different temperature.

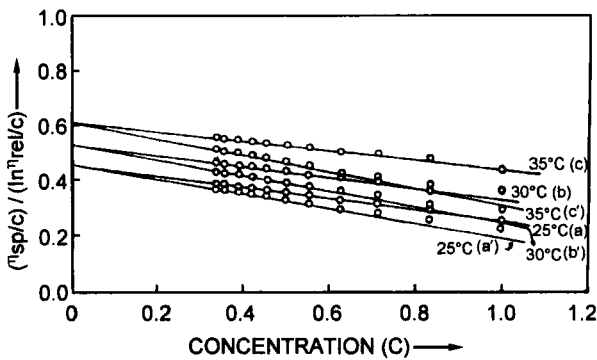


FIGURE 3  $\eta_{sp}/c(a, b, c)$  and  $\ln \eta_{rel}/c(a', b', c')$  plotted against concentration ( $c$ ) for Dextran ( $M_w = 75000$ ) in 50% Glucose at different temperature.

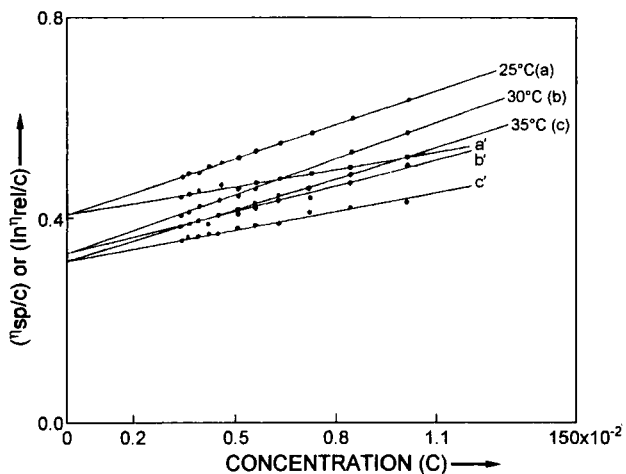


FIGURE 4  $\eta_{sp}/c(a, b, c)$  and  $\ln \eta_{rel}/c(a', b', c')$  plotted against concentration ( $c$ ) for Dextran ( $M_w = 250000$ ) in 6(M) Urea at different temperature.

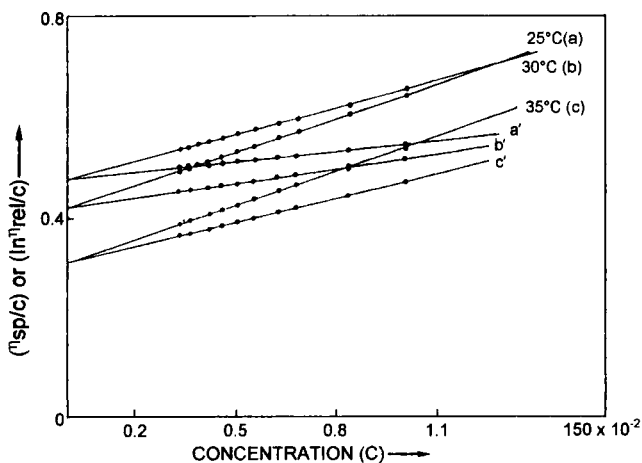


FIGURE 5  $\eta_{sp}/c(a, b, c)$  and  $\ln \eta_{rel}/c(a', b', c')$  plotted against concentration ( $c$ ) for Dextran ( $M_w = 250000$ ) in 2(M) Glycine at different temperature.

*i.e.*, ' $c = 0$ ', then the  $Y$ -axis intercept give the value of intrinsic viscosity  $[\eta]$  (according to Eq. (9)) and the slope of the curve gives the viscosity concentration coefficient ( $a_2$ ). Using Eq. (14) Huggins' constant ( $k_H'$ ) can be calculated for three different temperature and for three different solvents as shown in Tables I–III.



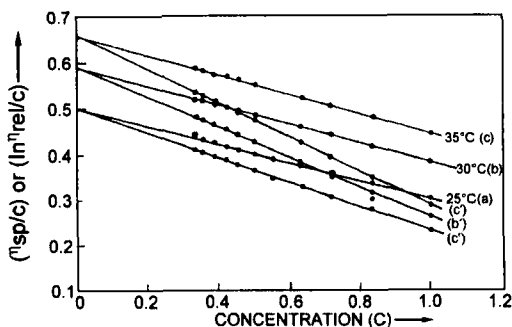


FIGURE 6  $\eta_{sp}/c$ (a, b, c) and  $\ln \eta_{rel}/c$ (a', b', c') plotted against concentration ( $c$ ) for Dextran ( $M_w = 250000$ ) in 50% Glucose at different temperature.

From the above plots we have drawn the following conclusions:

- (i) The intrinsic viscosity is more for Dextran of molecular weight 250000 in comparison to Dextran of molecular weight 75000. This is in agreement with the theory that for higher molecular weight, the intermolecular force of attraction being stronger, the viscosity will be higher.
- (ii) The viscosity concentration coefficient ( $a_2$ ) calculated by Eq. (11) is in good agreement with the experimental result obtained from the slope of the curve ( $\eta_{sp}/c$ ) versus ( $c$ ). But the deviation of experimental value of ( $a_2$ ) from the theoretical value increases as the temperature is raised. This might be due to the fact that the effect of temperature on intrinsic viscosity  $[\eta]$  has not been taken into consideration when deriving Eq. (11).
- (iii) The most remarkable conclusion from this study is that the intrinsic viscosity of the given polymer solution decreases with rise in temperature for solvents like Urea and Glycine but increases in the case of the solvent Glucose. The diametrically opposite behaviour of polymer Dextran in Glucose may be due to the non-polar character of Glucose, whereas the other two solvents—Urea and Glycine are polar in character. To confirm this we have taken some other polar solvents like Distilled water, NaOH and KOH and non-polar solvent Fructose. Another point to support this argument is that as the temperature rises (from 25°C to 35°C) the polymer swells more in the solvent Glucose leading to increase of intrinsic viscosity with increase in temperature for Glucose.

TABLE I Intrinsic viscosity  $[\eta]$ , Viscosity concentration coefficient ( $a_2$ ), Huggins' constant ( $k'_H$ ) and Kraemer's constant ( $k''_H$ ) of "Dextran" (of  $\bar{M}_w = 75000$  and 250000) in 6(M) Urea at 25°C, 30°C and 35°C

| Temp. in<br>°C | Intrinsic viscosity $[\eta]$ |                      | $a_2 = k'_H[\eta]^2$ (expt. value) |                      | $a_2 = .201[\eta]^{2.28}$ (theo. value) |                      | Huggins' constant ( $k'_H$ ) |                      | Kraemer's constant ( $k''_H$ ) |                      | $k'_H - k''_H$ |       |
|----------------|------------------------------|----------------------|------------------------------------|----------------------|---|----------------------|------------------------------|----------------------|--------------------------------|----------------------|----------------|-------|
|                | $\bar{M}_w = 75000$          | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$                | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$                     | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$          | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$            | $\bar{M}_w = 250000$ |                |       |
| 25             | 0.330                        | 0.407                | 0.117                              | 0.236                | 0.111                                   | 0.179                | 1.073                        | 1.425                | 0.532                          | 0.741                | 0.541          | 0.684 |
| 30             | 0.313                        | 0.326                | 0.111                              | 0.227                | 0.098                                   | 0.108                | 1.133                        | 2.136                | 0.551                          | 1.640                | 0.582          | 0.496 |
| 35             | 0.295                        | 0.313                | 0.094                              | 0.211                | 0.086                                   | 0.098                | 1.080                        | 2.150                | 0.448                          | 1.610                | 0.632          | 0.540 |

TABLE II. Intrinsic viscosity  $[\eta]$ , Viscosity concentration coefficient ( $a_2$ ), Huggins' constant ( $k'_H$ ) and Kraemer's constant ( $k''_H$ ) of "Dextran" (of  $\bar{M}_w = 75000$  and 250000) in 2(M) Glycine at 25°C, 30°C and 35°C

| Temp. in<br>°C | Intrinsic viscosity $[\eta]$ |                      | $a_2 = k'_H[\eta]^2$ (expt. value) |                      | $a_2 = 201[\eta]^{2.28}$ (theo. value) |                      | Huggins' constant ( $k'_H$ ) |                      | Kraemer's constant ( $k''_H$ ) |                      | $k'_H - k''_H$ |       |
|----------------|------------------------------|----------------------|------------------------------------|----------------------|--|----------------------|------------------------------|----------------------|--------------------------------|----------------------|----------------|-------|
|                | $\bar{M}_w = 75000$          | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$                | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$                    | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$          | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$            | $\bar{M}_w = 250000$ |                |       |
| 25             | 0.300                        | 0.480                | 0.119                              | 0.206                | 0.089                                  | 0.261                | 1.322                        | 0.894                | 0.856                          | 0.344                | 0.466          | 0.550 |
| 30             | 0.280                        | 0.420                | 0.095                              | 0.200                | 0.076                                  | 0.192                | 1.212                        | 1.138                | 0.744                          | 0.529                | 0.468          | 0.609 |
| 35             | 0.240                        | 0.313                | 0.086                              | 0.200                | 0.054                                  | 0.098                | 1.493                        | 2.041                | 0.816                          | 1.527                | 0.677          | 0.514 |

TABLE III Intrinsic viscosity  $[\eta]$ , Viscosity concentration coefficient ( $a_2$ ), Huggins' constant ( $k'_H$ ) and Kraemer's constant ( $k''_H$ ) of "Dextran" (of  $\bar{M}_w = 75000$  and 250000) in 50% Glucose at 25°C, 30°C and 35°C

| Temp. in<br>°C | Intrinsic viscosity $[\eta]$ |                      | $a_2 = k'_H[\eta]^2$ (expt. value) |                      | $a_2 = .201[\eta]^{2.28}$ (theo. value) |                      | Huggins' constant ( $k'_H$ ) |                      | Kraemer's constant ( $k''_H$ ) |                      | $k'_H - k''_H$ |       |
|----------------|------------------------------|----------------------|------------------------------------|----------------------|---|----------------------|------------------------------|----------------------|--------------------------------|----------------------|----------------|-------|
|                | $\bar{M}_w = 75000$          | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$                | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$                     | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$          | $\bar{M}_w = 250000$ | $\bar{M}_w = 75000$            | $\bar{M}_w = 250000$ |                |       |
| 25             | 0.455                        | 0.500                | 0.210                              | 0.216                | 0.231                                   | 0.286                | -1.014                       | -0.864               | -1.477                         | -1.412               | 0.463          | 0.548 |
| 30             | 0.530                        | 0.585                | 0.200                              | 0.212                | 0.327                                   | 0.410                | -0.712                       | -0.619               | -1.194                         | -1.096               | 0.482          | 0.477 |
| 35             | 0.610                        | 0.655                | 0.162                              | 0.206                | 0.451                                   | 0.530                | -0.435                       | -0.480               | -0.942                         | -0.965               | 0.507          | 0.485 |

- (iv) Comparing these curves with Huggins' equation we found that  $k'_H$  is positive for Dextran solution in Urea and Glycine but  $k'_H$  is negative for Glucose. This may be due to the fact that as Dextran is a polymer of Glucose, so in the polymer solution of Dextran in Glucose, there is a force of repulsion between solute (Dextran) and solvent (Glucose) which reduces the viscosity. With increase in dilution the force of repulsion reduces and hence the viscosity increases. This leads to the negative value of  $k'_H$ . But in the case of polymer solution of Dextran in Urea and Glycine, there is a force of attraction between solute (Dextran) and solvent (Urea and Glycine) which increases the viscosity and with increase in dilution the force of attraction reduces and hence the viscosity decreases.

In aqueous solutions of the polymer Dextran ( $\bar{M}_w = 75000$  and  $250000$ ) the plot of  $(\ln \eta_{rel}/c)$  versus  $(c)$  gives straight line as illustrated in Figures 1 to 6. These curves were extrapolated for infinite dilution *i.e.*,  $c=0$ , then the  $Y$ -axis intercept give the value of intrinsic viscosity  $[\eta]$  (according to Eq. (10)), and the slope of the curve divided by  $[\eta]^2$  give Kraemer's constant ( $k''_H$ ). Comparing the curves with Eq. (10) we found that  $k''_H$  is negative for Dextran solution in Glucose whereas positive for other two solvents *i.e.*, Urea and Glycine. It is a point of interest to record that  $k'_H - k''_H$  is found to be nearly 0.5 [15] for all the three solvents.

Thus from our present study we conclude that the viscosity behaviour of Glucose in Dextran exhibits an opposite trend in low temperature to that in higher temperature [8] whereas the other solvents—Urea and Glycine show identical trends both at higher and lower temperature.

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