

Viscosity studies of polyvinyl alcohol (PVA, $M_w = 1,25,000$) in solvent distilled water and aqueous solution of urea

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ABSTRACT

Reduced viscosity (η_{sp}/C) and inherent viscosity $\ln(\eta_{rel}/C)$ of PVA ($M_w = 1,25,000$) has been calculated by measuring the flow time of polymer solution in solvents like distilled water and 4M Urea at six different temperatures 25° C, 30° C, 35° C, 40° C, 45° C, and 50° C. From extrapolation of curve (η_{sp}/C) versus C and $(\ln \eta_{rel}/C)$ versus C , thermoviscosity parameters like Huggins' Constant (K_H^I), Kraemer's constant (K_H^{II}) and viscosity concentration co-efficient (a_2) have been estimated. In aqueous solution (PVA in distilled water), Huggins' relation does not hold good. So $a_2 = .201^{[\eta]^{2.28}}$ is used; but in aqueous Urea (PVA in 4M Urea), Huggins' relation holds good. Also $\eta = KM^a$ and value of a more for 4M Urea i.e. aqueous Urea is better solvent for PVA than distilled water.

Key words: Polyvinyl alcohol, distilled water, urea.

INTRODUCTION

Viscosity measurements of polymer solution shows the existence of molecular interaction between the polymer and the solvents. From these measurements, the extent of interaction can also be predicted. Solvation dynamics^{1,2} and its experimental and theoretical studies have given rise to renewed interest in the field of research activities³⁻⁶.

Several studies of the viscosity concentration relation of PVA in dilute aqueous solutions have been reported⁷ earlier, but their results do not agree and the causes of this discrepancy are unknown.

In the present study, the viscosity-concentration relation for PVA at six different temperatures are calculated. Generally, distilled water is used as solvent for PVA ($M_w = 1,25,000$) but since

it is a rather poor solvent, measurements are also made with solvent 4M Urea, which is expected to be a good solvent⁶.

EXPERIMENTAL

Requisites

Polymer

The polymer PVA of molecular weight ($M_w = 1,25,000$) is used as such without further purification.

Solvents

The solvents are distilled water and aqueous solution of (Urea BDH (AR) grade); used as such through out the experiment. A freshly prepared solution (1wt %) of the sample is prepared in solvent 4M Urea and Distilled water.

Viscometer

The 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.

The conditions for preparing aqueous solution of PVA are important, because they may exert a remarkable influence on the solution viscosity. When the dissolving time is less than 1 (one) hour at 100°C, the viscosity is highly time-dependent. When the time is more than 2 hours, the viscosity shows little change, but decreases gradually with time. This decrease can be ignored for time less than 5 hours. In our experiment, the dissolving time at 60°C is 8-10 hours and was standardised at about 1-2 hours at 100°C.

RESULTS AND DISCUSSION

In aqueous solution of PVA ($M_w = 1,25,000$), plots of $\eta_{sp}/C \sim C$ and $(\ln \eta_{rel})/C \sim C$ are straight lines (Fig. 1). In aqueous Urea both η_{sp}/C and $(\ln \eta_{rel})/C$ versus C also show the ordinary rectilinear relations (fig.2). But the slope of $(\ln \eta_{rel})/C$ versus C plot is negative in case of a aqueous Urea, where as it is positive in case of solvent distilled water.

The specific viscosity of the polymer solutions^{10,11} may be generally expressed as:

$$\eta_{sp} = a_1c + a_2c^2 + a_3c^3 \quad \dots(1)$$

Considering the dilute solutions, terms higher than the second order are neglected, giving

$$\eta_{sp}/C = a_1 + a_2C \quad \dots(2)$$

Table 1: Intrinsic viscosity [η], Viscosity concentration co-efficient (a_2), Huggins's Const. (K_H') of PVA ($M_w = 1,25,000$) in distilled water at temperatures ranging from 25°C to 50°C

Temp. in °C	Intrinsic viscosity ^(η)	$a_2 = K_H'[\eta]^2$ (expt. value)	$a_2 = .201 \times [\eta]^{2.28}$ (theo. value)	Huggins' constant (K_H')
25	0.760	0.539	0.744	0.933
30	0.635	0.486	0.494	1.205
35	0.580	0.405	0.402	1.204
40	0.537	0.421	0.337	1.460
45	0.467	0.313	0.245	1.435
50	0.433	0.345	0.206	1.804

Table 2: Intrinsic Viscosity [η], Viscosity concentration co-efficient (a_2), Huggins' const (K_H'), Mead-Fuoss Const. (β) of PVA ($M_w = 1, 25, 000$) in 4M Urea at temperatures ranging form 25°C to 50°C.

Temp. in in °C	Intrinsic Viscosity ^(η)	$a_2 = K_H'[\eta]^2$ (expt. vlaue)	Huggins' const. (K_H')	β	$K_H' + b$
25	1.041	0.513	0.473	0.090	0.563
30	0.990	0.469	0.479	0.097	0.576
35	0.895	0.349	0.436	0.105	0.541
40	0.842	0.370	0.522	0.056	0.578
45	0.765	0.325	0.554	0.017	0.572
50	0.733	0.280	0.521	0.054	0.575

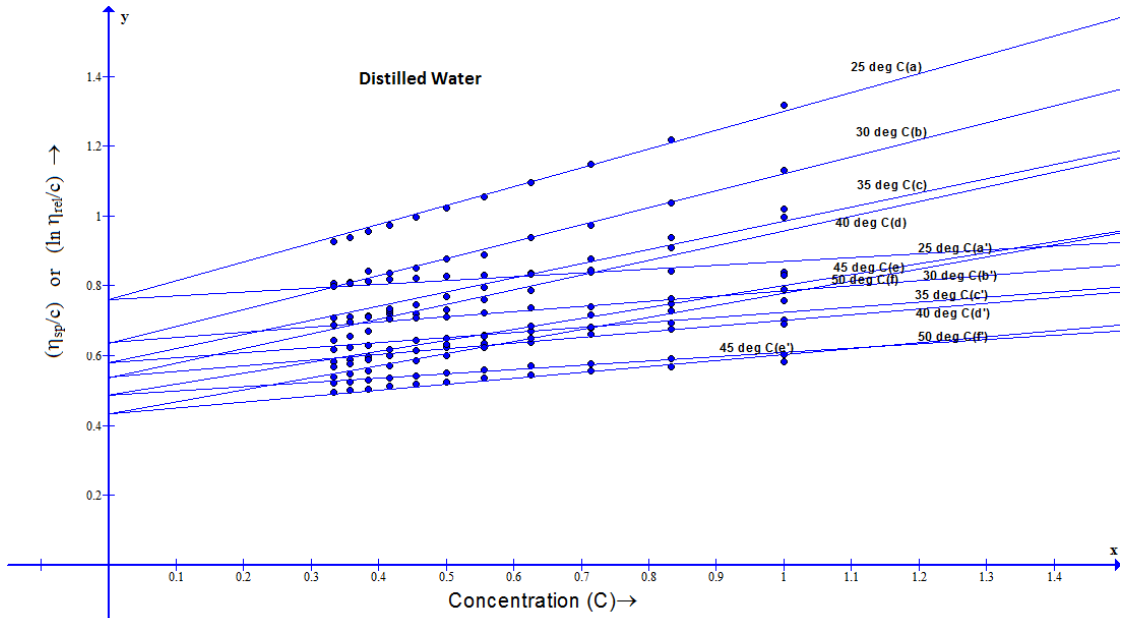


Fig. 1: η_{sp}/c (a,b,c,d,e,f) and η_{rel}/C (a',b',c',d',e',f') plotted against concentration (c) for PVA ($M_w=1,25,000$) in distilled water at different temperature

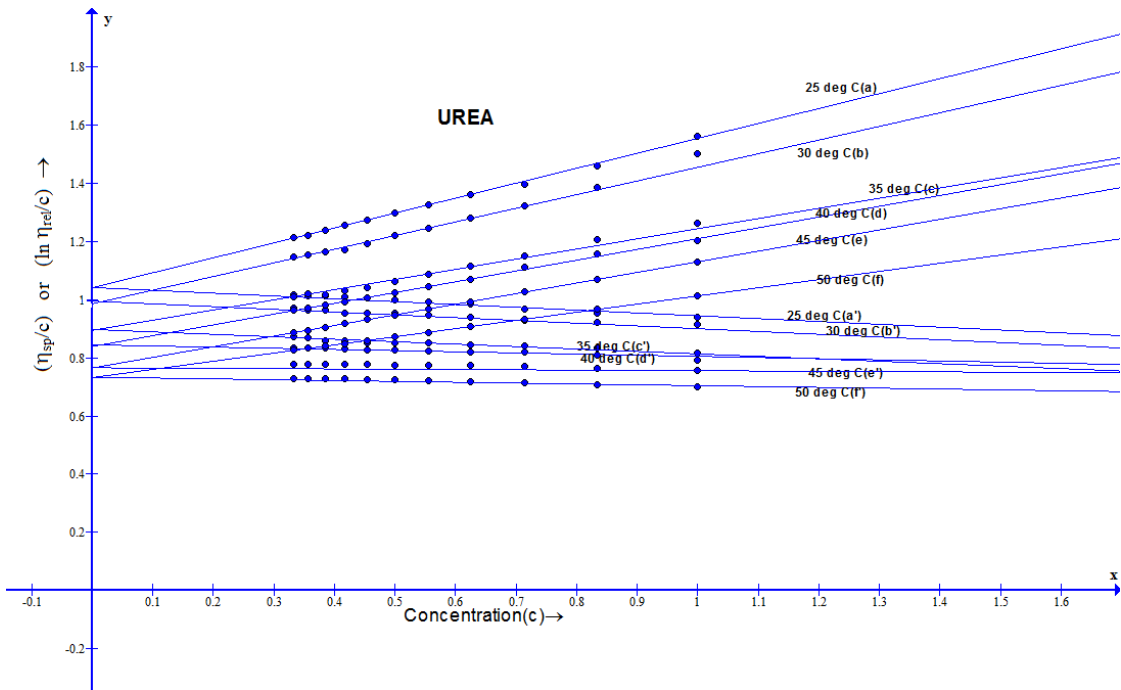


Fig. 2: η_{sp}/c (a,b,c,d,e,f) and η_{rel}/C (a',b',c',d',e',f') plotted against concentration (c) for PVA ($M_w=1,25,000$) 4M Urea at different temperature

According to Huggins¹¹,

$$a_2 = K_H[\eta]^2 \quad \dots(3)$$

$$\text{So that } \eta_{sp}/C = [\eta] + K_H[\eta]^2C \quad \dots(4)$$

Values of a_2 and K_H estimated from the viscosity measurements of PVA ($M_w = 1,25,000$) in aqueous solution and in 4M Urea are shown in Table 1 and 2.

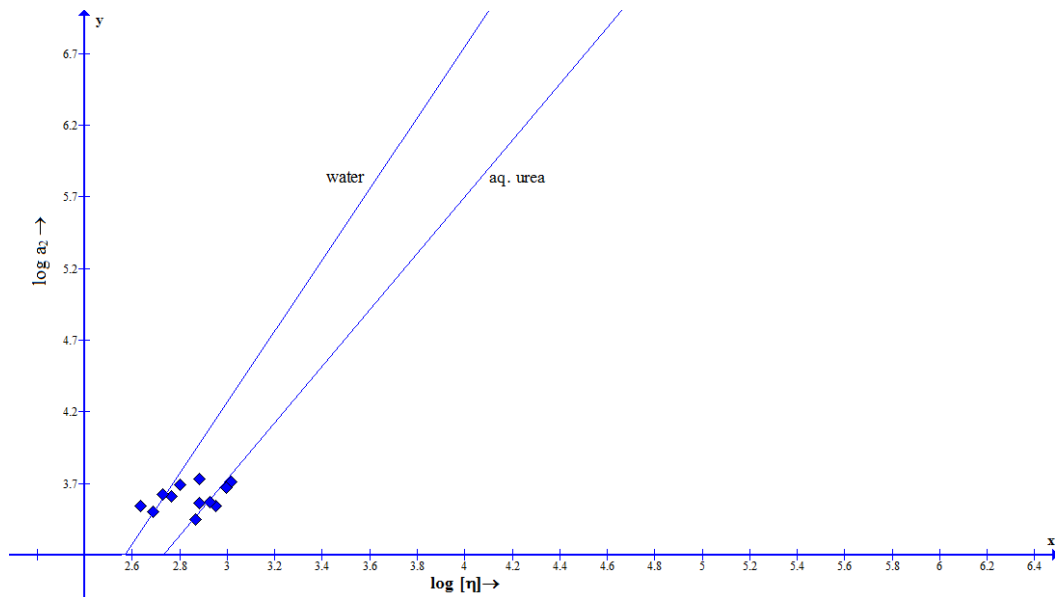


Fig. 3: $\log a_2$ plotted against $\log[\eta](c)$ for PVA ($M_w=1,25,000$) in aqueous and in aqueous urea solutions

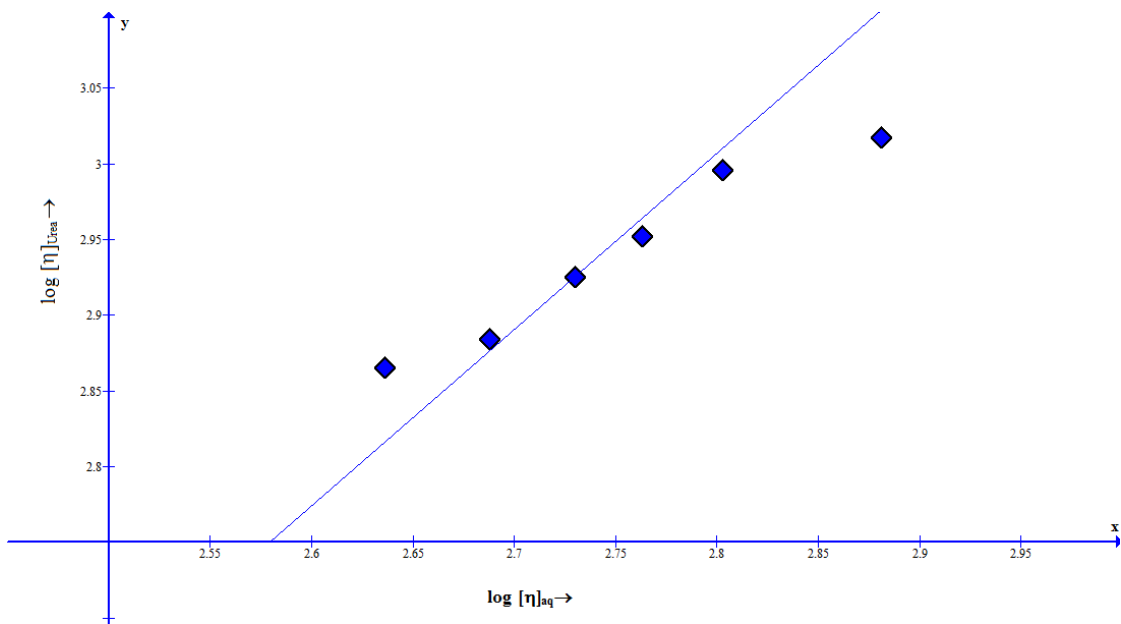


Fig. 4: $\log[\eta]_{\text{Urea}}$ plotted against $\log[\eta]_{\text{aq}}$ for PVA ($M_w=1,25,000$)

The results appear in Fig. 3, where $\log a_2$ is plotted against $\log [\eta]$ for both aqueous and aqueous Urea solutions. In each case, a rectilinear relation is well realised, but the slope differs in each system. In aqueous Urea, the slope is $a_2 = K_H'[\eta]^2$, according to Huggins' formula; but in aqueous solution the slope is higher, corresponding to

$$a_2 = 0.201 \times [\eta]^{2.28} \quad \dots(5)$$

The evaluated values of a_2 from eq. (5) are shown in Table 1 and are in good agreement with experimental values.

In the aqueous urea, the Mead Fuoss equation¹²

$$\ln \eta_{ref}/C = [\eta] - \beta[\eta]^2 C$$

Table 3: Log $[\eta]$, Log a_2 for aqueous solution and aqueous Urea at temperatures ranging from 25°C to 50°C

Temp. in In °C	Aqueous Solution		Aqueous Urea	
	log $[\eta]$ (ml/g)	Log $a_2 \times 10^{-4}$	log $[\eta]$ (ml/g)	log $a_2 \times 10^{-4}$
25	2.881	3.73	3.017	3.71
30	2.803	3.69	2.996	3.67
35	2.763	3.61	2.952	3.54
40	2.730	3.62	2.925	3.57
45	2.688	3.50	2.884	3.56
50	2.636	3.54	2.865	3.45

in good agreement with experiment. Some examples of b are illustrated with K_H' in Table 2. The sum of K_H' and b (Mead-Fuoss const.) agree well with the theoretical value 0.5.

The relation between the intrinsic viscosity in the aqueous Urea and in aqueous solution is illustrated in a log-log plot given in fig. 4.

From fig. 4, the following empirical formula is obtained

$$[\eta]_{Urea} = 1.7[\eta]_{aq}^{1.164}$$

In which $[\eta]_{Urea}$ and $[\eta]_{aq}$ are the intrinsic

viscosities of PVA ($M_w = 1,25,000$) in the aqueous Urea and in the aqueous solution, respectively. This means that, the exponent α of the Sakurada-Houwink equation, $[\eta] = KM^\alpha$, is higher in the aqueous Urea than in the aqueous solutions i.e. the aqueous Urea is a better solvent than water.

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