

## Viscosity Parameters and Energy of Activation of Dilute Aqueous Polyvinyl Alcohol (PVOH) Solutions

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**Summary:** The viscometric behaviour of aqueous dilute solutions of polyvinyl alcohol (PVOH) of varying polymer concentration (0.1g/dL-1.0g/dL) and temperature (10 -80°C) has been studied. Rapid increase in solution viscosity with increase in PVOH concentration are obviously related to polymer nonsphericity and the tendency of molecules to experience extensive nonhydrodynamic interaction. The intrinsic viscosities were obtained by using Huggins equation. By applying the Mark-Houwink expression the "viscosity average molecular weight" was determined. Curves were obtained when values of reduced viscosity vs. temperature were plotted except for 0.1 and 0.2g/dL solution where straight lines with negative slopes were attained. The values of pre-exponential factor A and the apparent activation energy of viscous flow  $E_a$  were obtained by plotting  $\ln \eta_{sp}/c$  vs.  $1/T$ .

### Introduction

The polyvinyl alcohol [1,2] is a linear polymer hereafter denoted as PVOH. Different experimental techniques are used for characterizing the polymer solutions like viscometry, light scattering, osmometry and IR studies etc. The viscometric method has been employed extensively due to its simplicity and high sensitivity to aggregation [3,4] phenomenon. The poiseuille equation [5-7] is modified and for a relative viscosity of a solution, it changes to the simplest form

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \quad \text{----- 1}$$

where  $\eta$  and  $\eta_0$  are the viscosities of sample and reference liquid respectively,  $t$  and  $t_0$  are the time of flow

for the same volumes of the respective liquids in the same viscometer.

Polymers both natural and synthetic have generally molecules which are not spherical but either rod-like or flexible chainlike [5,8] and thus specific viscosity  $\eta_{sp}$  ( $\eta_{sp}/c$ ) increase more rapidly with concentration than is indicated by the Einstein's relation [8], namely,

$$\eta_{sp} = kc \quad \text{----- 2}$$

where  $c$  is the concentration in g/dL of solution. In dilute polymer solutions the change of reduced viscosity ( $\eta_{red} = \eta_{sp}/c$ ) with concentration is generally expressed according to the well known Huggins equation [2,6].

$$\eta_{sp} = [\eta]_{int} + k_H [\eta]_{int}^2 c \quad (3)$$

where  $k_H$  is known as Huggins constants and  $[\eta]_{int}$  is the viscosity number of intrinsic viscosity. The plot of  $\eta_{sp}/c$  versus concentration (eq. 3) is extrapolated to zero concentration, where the intercept gives the value of intrinsic viscosity  $[\eta]_{int}$ . For estimating the "viscosity average molecular weight",  $M_v$ , we utilized the Mark-Houwink relation [2,4,5].

$$[\eta]_{int} = K M_v^a \quad (4)$$

where at a given temperature  $K$  and  $a$  are constants for a specific polymer in a specific solvent.

The temperature dependence of the actual viscosity [2,9]  $\eta$  of dilute polymer solutions may be expressed by the well known Arrhenius expression [10,11]:

$$\eta = A \exp(E_a/RT) \quad (5)$$

where  $E_a$  is the apparent activation energy of the flow process and  $A$  a pre-exponential factor.

## Experimental

### Material

The polymer samples used in this work is polyvinyl alcohol PVOH (Trade Mark-PX-1295-3 U.S.A.) of MCB Manufacturing Chemists, Inc. It is readily soluble in water at a temperature of 80°C. All of the solutions were prepared and used freshly to prevent the supermolecule structure formation [12,13] due to long term storage. The viscosity of a 4% solution at 20°C

ranges from 28-32 cps as determined by Rotary viscometer (model BM viscometer type A of Ogawa Seiki Ltd.).

### Procedure

The solutions of PVOH in distilled water were prepared at 80°C. The concentration investigated ranged from 0.1 to 1.0g/dL. The temperature was maintained constant for a particular measurement. Fluctuations of the temperature were less than  $\pm 0.04^\circ\text{C}$ . The viscosities of all ten samples (0.1 - 1.0g/dL) were measured at temperatures of 10, 20, 30, 40, 50, 60, 70 and 80°C.

## Results and Discussion

The values of relative viscosities were used to determine the specific viscosities of the samples at experimental temperatures. The values of reduced viscosity  $\eta_{sp}/c$  vs. concentration  $c$  were plotted for each temperature range varying from 10 to 80°C.

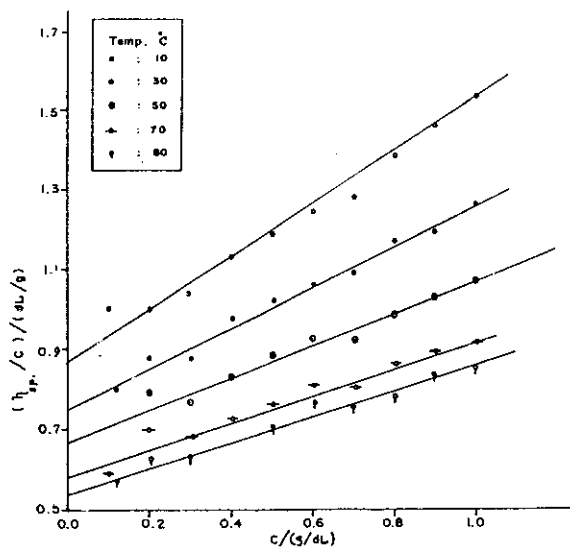


Fig.1: Change of reduced viscosity  $\eta_{sp}/C$  of aqueous polyvinyl alcohol (PVOH), solutions with concentration  $C$  for different temperatures.

Table-1: Reduced Viscosity  $\eta_{sp}/c$  as a function of concentration  $c$  and temperature

PVOH (g/dL)	10°C	20°C	30°C	$\eta_{sp}/c$ 40°C	50°C	60°C	70°C	80°C
0.1	1.015	0.81	0.80	0.70	0.80	0.67	0.59	0.58
0.2	1.005	0.975	0.895	0.835	0.79	0.725	0.70	0.63
0.3	1.036	0.956	0.886	0.806	0.766	0.726	0.68	0.636
0.4	1.125	1.057	0.98	0.905	0.835	0.78	0.727	-
0.5	1.208	1.124	1.03	0.954	0.89	0.812	0.764	0.708
0.6	1.245	1.168	1.075	0.997	0.926	0.865	0.81	0.765
0.7	1.278	1.196	1.093	1.003	0.927	0.863	0.803	0.758
0.8	1.387	1.252	1.172	1.080	0.989	0.912	0.856	0.795
0.9	1.46	1.331	1.206	1.113	1.03	0.960	0.893	0.836
1.0	1.534	1.398	1.263	1.163	1.075	0.990	0.929	0.853

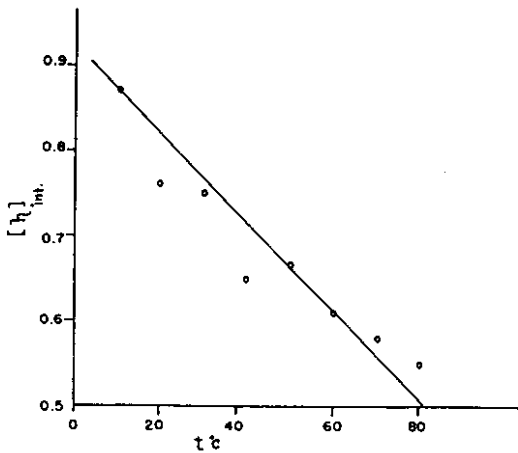


Fig.2: Variation of intrinsic viscosity  $[\eta]_{int}$  with temperature °C.

Table-II: Intrinsic Viscosity  $[\eta]_{int}$  and Huggins Constant  $k_H$  at different temperature

$t(c,0)$	$[\eta]_{int}$	Slope	$k_H = \text{Slope}/[\eta]_{int}^2$
10	0.87	0.666	0.88
20	0.76	0.625	1.08
30	0.75	0.52	0.91
40	0.65	0.50	1.18
50	0.67	0.405	0.90
60	0.61	0.389	1.04
70	0.58	0.333	1.00
80	0.55	0.314	1.04

The plots of  $\eta_{sp}/c$  vs.  $c$  yield intrinsic viscosity  $[\eta]_{int}$  value at each temperature according to equation 3. Table I contains the values of reduced viscosity for each sample studied as a

function of temperature. The representative plots of  $\eta_{sp}/c$  vs.  $c$  for 10,30,50,70 and 80°C are shown in Fig. 1. The values of intrinsic viscosity  $[\eta]_{int}$  i.e. intercept at zero concentration at all the experimental temperature are given in table II. The slopes of the plots and values of  $k_H$  (Huggins constant) are also given in the same table. It is noted that, in general, the values of  $k_H$  increases with increase of temperature. In Fig. 2 the values of  $[\eta]_{int}$  are plotted against the temperature (°C). The plot is a straight line. The decrease of  $[\eta]_{int}$  and increase of  $k_H$  with temperature indicates that as the temperature of the sample solution increases the size of the individual polymer molecules

(monomolecular) decreases and interaction among polymer molecules increases [12-15]. The values of  $\eta_{sp}/c$  are also plotted vs. temperature (°C) for all samples of PVOH investigated, in all cases smooth curves were obtained except 0.1 and 0.2g/dL where linear graphs of negative slopes were attained. The representative plots of  $\eta_{sp}/c$  vs. temperature are shown in Fig. 3. The Mark-Houwink equation was used for estimation of "Viscosity average molecular weight"  $M_v$  of PVOH [2,16] in water at 30°C.

$$[\eta]_{int} = 33.88 \times 10^{-5} M_v^{0.716}$$

The molecular weight thus found was approximately 47000. The values of  $\ln \eta$  at different absolute tempera-

Table-III: The values of  $\ln \eta$  as a function of absolute temperature  $T$  and concentration

PVOH (g/dL)	283K	293K	303K	313K	323K	333K	343K	353K
0.1	0.3636	0.0805	-0.1468	-0.3548	-0.5280	-0.6981	-0.8491	-0.9867
0.2	0.4501	0.1802	-0.0599	-0.2684	-0.4585	-0.6279	-0.7753	-0.9250
0.3	0.5382	0.2543	0.0114	-0.2057	-0.3984	-0.5662	-0.7202	-0.8690
0.4	0.6385	0.3551	0.1066	-0.1136	-0.3173	-0.4911	-0.651	-
0.5	0.7396	0.4485	0.1908	-0.0331	-0.2372	-0.4226	-0.5829	-0.7409
0.6	0.8249	0.5334	0.2735	0.0458	-0.1635	-0.3446	0.5104	-0.6660
0.7	0.9063	0.6103	0.3439	0.1087	-0.1053	-0.2905	-0.4601	-0.6177
0.8	1.0139	0.7064	0.4374	0.2001	-0.022	-0.2146	-0.3846	-0.5512
0.9	1.1058	0.7898	0.5110	0.2712	0.0503	-0.1404	-0.3162	-0.4825
1.0	1.1967	0.8767	0.5923	0.3485	0.1245	-0.0747	-0.2494	-0.4295

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0.5	0.7396	0.4485	0.1908	-0.0331	-0.2372	-0.4226	-0.5829	-0.7409
0.6	0.8249	0.5334	0.2735	0.0458	-0.1635	-0.3446	0.5104	-0.6660
0.7	0.9063	0.6103	0.3439	0.1087	-0.1053	-0.2905	-0.4601	-0.6177
0.8	1.0139	0.7064	0.4374	0.2001	-0.022	-0.2146	-0.3846	-0.5512
0.9	1.1058	0.7898	0.5110	0.2712	0.0503	-0.1404	-0.3162	-0.4825
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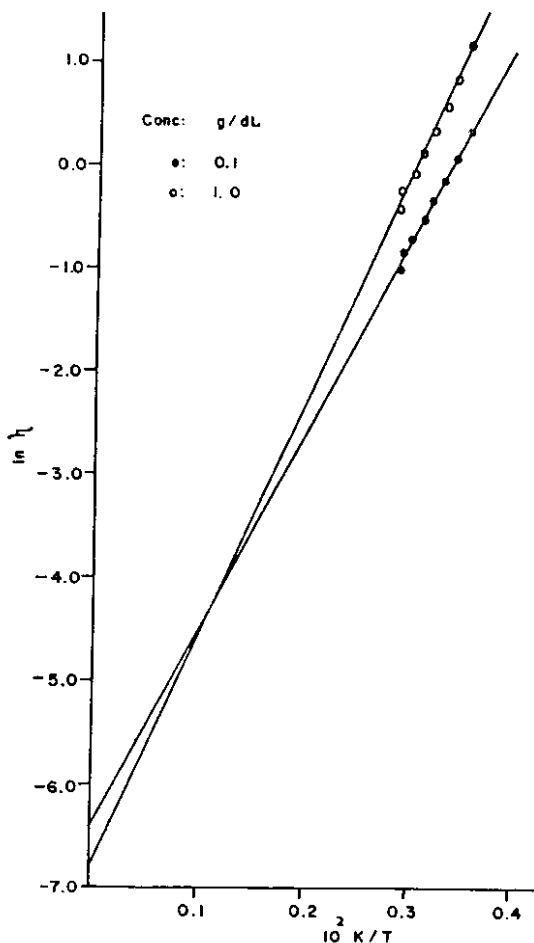


Fig.3: Representative plots of  $\ln \eta$  as a function of  $1/T$  for two samples of PVOH.

ture,  $T$ , for all concentrations investigated are given in Table III. Fig. 4 shows typical plots of  $\ln \eta$  vs.  $1/T$  for only the lowest (0.1g/dL) and highest (1.0g/dL) concentrations. All the plots of  $\ln \eta$  vs.  $1/T$  for all samples were strictly linear over the temperature range employed. The values of apparent activation energy  $E_a$  of viscous flow and pre-exponential factor  $A$  (Eq.5) obtained by plotting  $\ln \eta$  vs.  $1/T$  for different samples of PVOH studied are given in table 4. The table indicates that within experimental error, the values of  $E_a$  increases and of  $A$  decreases but not systematically with concentration, which is according to expectation [11,17].

Table-IV: The values of apparent activation energy of viscous flow  $E_a$  and pre-exponential factor  $A$ .

PVOH (g/dL)	$E_a$ (kJ mol <sup>-1</sup> )	$A \times 10^2$
0.1	15.8	0.16
0.2	16.4	0.13
0.3	16.6	0.12
0.4	16.8	0.15
0.5	17.4	0.10
0.6	17.3	0.13
0.7	17.6	0.11
0.8	17.9	0.12
0.9	18.2	0.12
1.0	18.7	0.11

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