

# Effect of Temperature on the Viscosity of Dilute Polyelectrolyte Solutions

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**Summary:** We report the effect of temperature on the viscosity of dilute polyelectrolyte solutions. It has been observed that the reduced viscosity increases with dilution, reaches to a maximum and then decreases in the limit of infinite dilution. Moreover, the maximum decreases and shifts towards higher polymer concentration with increase in temperature. Thermodynamic parameters of viscous flow ( $\Delta G_v$ ,  $\Delta H_v$ ,  $\Delta S_v$ ) have also been calculated and discussed.

## Introduction

Polyelectrolytes constitute the class of polymers which bear a large number of ionizable groups on the main chain [1,2]. Thus they possess the properties of both the polymers and electrolytes. Over the past few decades there has been a growing body of theoretical and experimental literature concerning the solution properties of polyelectrolytes [3]. The presence of ionic groups in polyelectrolytes result in strong inter and intra molecular coulombic interactions due to which their solution behaviour is different than the ordinary polymers. General consensus, until very recently, was that the reduced viscosity of the polyelectrolyte solutions would increase without bound with dilution. However, more careful investigations on dilute solutions of polystyrene sulfonate [4] have revealed that the reduced viscosity passes through a maximum with dilution and the neutral polymer behaviour is observed in the limit of infinite dilution. These studies revealed that the qualitative behaviour of the reduced viscosity is not affected by charge on the counterion. Increasing charge on the counterion decreases the maximum and shifts it to higher polymer concentration.

Most of the previous viscosity data has been reported at room temperature. Since temperature

plays a significant role in the determination of both the inter and intra molecular interactions, in the present study we have considered this aspect. In this paper we report the dilute solution viscosities of aqueous polystyrene sulfonate solutions in the temperature range 288-328 K. We also report, for the first time, the thermodynamic parameters of viscous flow *viz.*  $\Delta H_v$ ,  $\Delta G_v$  and  $\Delta S_v$  of these solutions.

## Results and Discussion

In Figure 1 a plot of the reduced viscosity versus concentration for aqueous polystyrene sulfonate solutions is shown at different temperatures. This figure shows a behaviour typical of polyelectrolytes i.e. the reduced viscosity increases with dilution, reaches to a maximum and then decreases in the limit of infinite dilution. A similar behaviour has previously been reported by Cohen *et al.* [5] for the same system. The figure also shows a decrease in the maximum with increase in temperature. Similarly the position of the maximum shifts slightly towards high polymer concentration with increase in temperature. Thus at 328 K, the maximum occurs at  $1.6 \times 10^{-5}$  gm/ml as compared to that at 288 K which occurs at  $1 \times 10^{-5}$  gm/ml. Moreover, decrease in the reduced

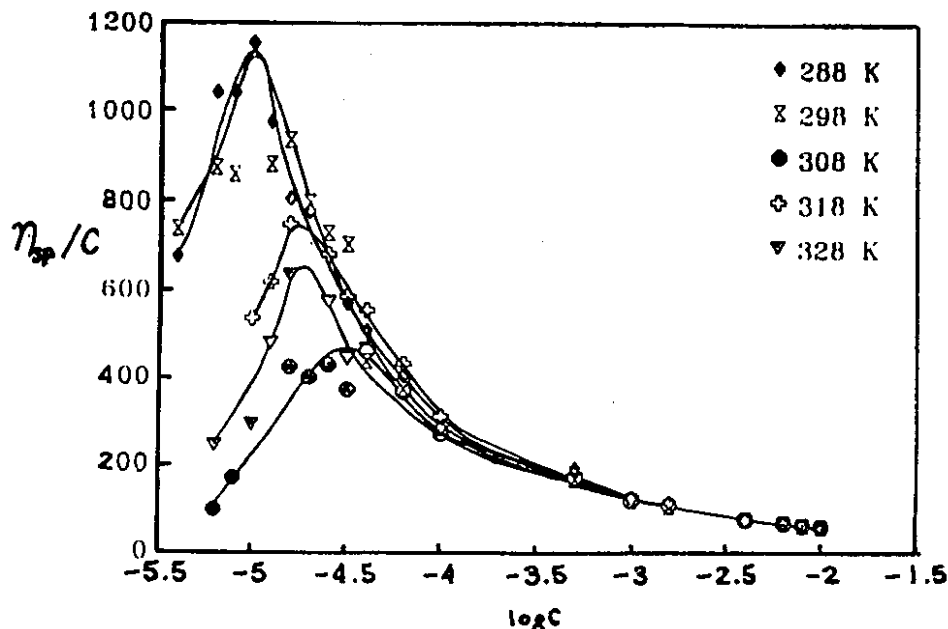


Fig. 1: Plot of  $\eta_{sp}/C$  versus  $\log C$  for various aq. NaPSS solutions containing no salt at different temperature.

viscosity with increase in temperature is more pronounced as compared to that above the  $C_{max}$ . The curves start to coalesce at  $C=1 \times 10^{-4}$  gm/ml and above this concentration no appreciable temperature effect is noted. Significant decrease in reduced viscosity with increase in temperature in the region below  $C_{max}$  may be due to the fact that increase in the free volume is greater than the chain expansion in this region. Thus an overall decrease in the reduce viscosity is observed. On the other hand, in the region above  $C_{max}$ , due to higher concentration, chain expansion and free volume increase counterbalance each other with a net result of no effect on the  $\eta_{sp}/C$ .

Thermodynamic parameters of viscous flow viz,  $\Delta G_v$ ,  $\Delta H_v$  and  $\Delta S_v$  were calculated using the Frenkel-Eyring [7] equation in the form

$$\ln \eta = \left( \ln A - \frac{\Delta S_v}{R} \right) + \frac{\Delta H_v}{RT} \quad (3)$$

where A is the preexponential factor and has been reported to have a constant value of  $10^3$  poise for all liquids [7]. Figure 2 shows a plot of  $\ln \eta$  versus  $1/T$  for different concentrations of polystyrene sulfonate. From the slope and intercept of the lines, values of

$\Delta H_v$  and  $\Delta S_v$  were determined. These values are listed in Table 1. Using these values of  $\Delta H_v$  and  $\Delta S_v$  free energy of activation of viscous flow as calculated by the equation

$$\Delta G_v = \Delta H_v - T\Delta S_v \quad (4)$$

and its values at different temperatures and concentrations are listed in Table 2. Since the value of  $\Delta H_v$ , is independent of temperature and concentration, its average value  $16.28 \pm 0.09$  has been used in the above calculations.

Table 1: Thermodynamic parameters of viscous flow for aqueous polystyrene sulfonate solutions at different concentrations.

Concentration (gm/ml)	$\Delta H_v$ (KJ mol <sup>-1</sup> )	$-\Delta S_v$ (J mol <sup>-1</sup> K <sup>-1</sup> )
$1 \times 10^{-5}$	16.29	2.039
$2.5 \times 10^{-5}$	16.46	1.508
$7 \times 10^{-5}$	16.39	1.803
$5 \times 10^{-4}$	16.24	2.456
$1.5 \times 10^{-3}$	16.25	3.330
$4 \times 10^{-3}$	16.15	4.718
$8 \times 10^{-3}$	16.22	5.029
$1 \times 10^{-2}$	16.24	5.336

Average value of  $\Delta H_v = 16.28 \pm 0.09$

Table 2: Values of the free energy of viscous flow ( $\Delta G_v$ ,  $\text{KJ. mol}^{-1}$ ) at different temperatures for aqueous polystyrene sulfonate solutions.

Concentration (gm/ml)	Temperature (K)				
	288	298	308	318	328
$1 \times 10^{-5}$	16.88	16.89	16.92	16.94	16.96
$2.5 \times 10^{-5}$	16.89	16.91	16.92	16.94	16.95
$7 \times 10^{-5}$	16.91	16.93	16.95	16.96	16.98
$5 \times 10^{-4}$	16.94	16.97	16.99	17.02	17.05
$1.5 \times 10^{-3}$	17.21	17.23	17.27	17.29	17.33
$4 \times 10^{-3}$	17.51	17.56	17.60	17.65	17.69
$8 \times 10^{-3}$	17.67	17.72	17.77	17.82	17.87
$1 \times 10^{-2}$	17.78	17.83	17.88	17.94	17.99

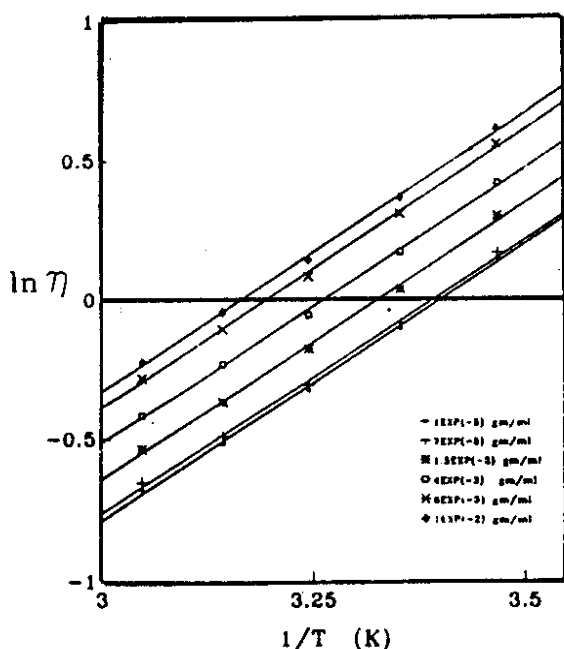


Fig. 2: Plot of  $\ln \eta$  versus  $1/T$  of aqueous polystyrene sulfonate solutions without added salt.

The amount of energy required by a segment to jump from one equilibrium position to the other is known as the potential energy barrier [6]. The height of this barrier is characterized by  $\Delta H_v$ . In figure 3 we show a plot of  $\Delta G_v$ , versus temperature. It can be seen that  $\Delta G_v$ , increases with increase in concentration and does not change appreciably with temperature. The increase in  $\Delta G_v$ , with increase in concentration may be interpreted in terms of the lower free space available to the polymer segments at higher concentrations. Thus the segments would be expected to require more energy in order to jump from one equilibrium position to the other.

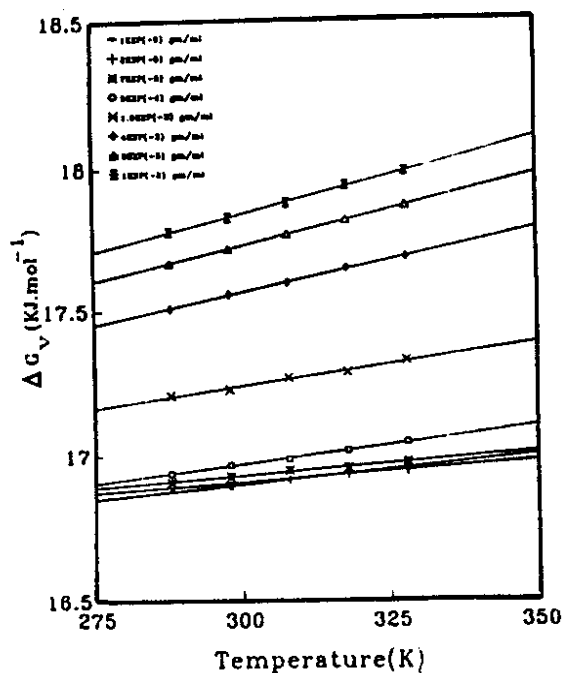


Fig. 3: Plot of free energy of viscous flow of aqueous NaPSS solutions without added salt against temperature.

Table 3: Values of the entropy of viscous flow ( $-\Delta S_v$ ,  $\text{J. mol}^{-1}$ ) of aqueous polystyrene sulfonate solutions at different concentrations and temperatures.

Concentration (gm/ml)	Temperature (K)				
	288	298	308	318	328
$1 \times 10^{-5}$	2.08	2.05	2.08	2.08	2.07
$2.5 \times 10^{-5}$	2.12	2.11	2.08	2.08	2.04
$7 \times 10^{-5}$	2.19	2.18	2.18	2.14	2.13
$5 \times 10^{-4}$	2.29	2.32	2.31	2.33	2.35
$1.5 \times 10^{-3}$	3.23	3.19	3.21	3.18	3.20
$4 \times 10^{-3}$	4.27	4.29	4.29	4.31	4.30
$8 \times 10^{-3}$	4.83	4.83	4.84	4.84	4.85
$1 \times 10^{-2}$	5.21	5.20	5.19	5.22	5.21

Values of  $\Delta S_v$ , determined from the plot of  $\ln \eta$  versus  $1/T$  are listed in Table 1. In Table 3 values of  $\Delta S_v$ , calculated through equation 4 are listed. It can be seen that both the calculated and experimentally determined values are in good agreement. Entropy is a function directly linked with the degree of order in a system and its diminution points to a gain of order [6]. Negative values of  $\Delta S_v$ , observed for the present system may be due to uncoiling and orientation of the polymer molecules which occur during the course of

flow. The data also shows that like  $\Delta H_v$ ,  $\Delta S_v$ , is independent of temperature. This shows that NaPSS molecules are unassociated in the concentration range studied.

### Experimental

Poly(sodium-4-styrene sulfonate) abbreviated as NaPSS,  $M_w=70,00$  was obtained from Aldrich Chemical Company Inc., USA. All the solutions were made in doubly distilled water. A stock solution of the highest concentration was first prepared. All other solutions were prepared by adding appropriate amount of the solvent to the stock solution. For viscosity measurements Ostwald viscometer with flow time of 270 seconds for the solvent at 25 °C was used. The flow times of all the solutions were such that no kinetic energy correction was required. A digital stopwatch was used for measuring the flow times of the solutions with an accuracy of  $\pm 0.01$  seconds. The temperature was controlled with a thermostat. A digital thermometer with an accuracy of  $\pm 0.1$  °C was also used in order to keep a strict check on the temperature fluctuations. Densities of all the solutions were measured by a calibrated pycnometer made in our laboratory.

From the flow times and density of each solution, absolute viscosity (centipoise, cP) was calculated using the equation

$$\eta = \rho Bt \quad (1)$$

where  $\rho$  and  $t$  are the density (g/ml) and flow time (seconds) of solution respectively and  $B$  is viscometer constant.

$$\text{Specific viscosity } (\eta_{sp}) = \frac{t_s}{t_0} - 1 \quad (2)$$

where  $t_s$  and  $t_0$  are the flow times of the solution and solvent respectively.

Table 4: Absolute viscosity ( $\eta$ , centi Poise) of aqueous polystyrene sulfonate solutions at different temperatures and concentrations without added salt

Concentration (g/ml)	Absolute viscosity ( $\eta$ , cP)				
	288K	298K	308K	318K	328K
$1 \times 10^{-5}$	1.158	0.902	0.726	0.598	0.507
$2.5 \times 10^{-5}$	1.176	0.909	0.728	0.603	0.509
$7 \times 10^{-5}$	1.178	0.918	0.739	0.613	0.520
$5 \times 10^{-5}$	1.260	0.973	0.795	0.652	0.550
$1.5 \times 10^{-3}$	1.344	1.036	0.840	0.695	0.586
$4 \times 10^{-3}$	1.512	1.183	0.947	0.797	0.662
$8 \times 10^{-3}$	1.736	1.355	1.086	0.901	0.758
$1 \times 10^{-2}$	1.837	1.436	1.152	0.957	0.803

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