

# Effect of Counterion Charge on the Viscosity of Dilute Polyelectrolyte Solutions

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**Summary:** Effect of counter ion charge (cation of the added salt) on the viscosity of dilute aqueous sodium polystyrene sulfonate solutions has been studied. It has been observed that for solutions without added salt the reduced viscosity increases with dilution, reaches to a maximum and then decreases in the limit of infinite dilution. In the presence of added salt the height of the maximum decreases and shifts towards higher polymer concentration in the following order  $AlCl_3 > CaCl_2 > NaCl$

## Introduction

Dilute solution properties of polyelectrolytes are of interest, both theoretically and experimentally, due to their unusual behaviour as compared to the solutions of natural polymers. The presence of charged groups on the main chain make the polyelectrolytes behave differently under varying experimental conditions. Most of the previous viscosity studies showed that viscosity of polyelectrolyte solutions increases without bound in

the limit of infinite dilution. Thus extrapolations to zero concentration, required for the estimation of intrinsic viscosity, were difficult. These results were explained on the basis that at extreme dilution, the chains fully expand and behave as rigid rods instead of coils. Recently, however, more careful investigation [1,2] have shown that the behaviour of extremely dilute solutions of polyelectrolytes is different. These studies revealed

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that the reduced viscosity increases with dilution, passes through a maximum and then decreases with further dilution. Eventually the neutral polymer behaviour is recovered in the limit of infinite dilution. These studies have been reported both for systems with and without added salts. Effect of the counter ion charge on the reduced viscosity has also been reported [1] for polystyrene sulfonate solutions. The salts studied were NaCl,  $MgSO_4$  and  $La(NO_3)_3$ .

In these salts the size of the anions and the cations is different, which makes any comparison of the observed effects difficult. The present study was, therefore, undertaken by using salts with different cations but the same anion. Thus any effect due to variation in the size of the anion becomes negligible. The salts studied are NaCl,  $CaCl_2$  and  $AlCl_3$ .

### Results and Discussion

Figure 1 shows a plot of reduced viscosity versus concentration of the aqueous solution of NaPSS without added salt at 25°C. This figure shows a behaviour typical of polyelectrolyte solution i.e.  $\eta_{sp}/C_p$  increases with dilution, reaches to a maximum and then decreases in the limit of extreme dilution. We have observed a maximum at  $C_p = 1 \times 10^{-5}$  gm/ml. Below this concentration there is an abrupt decrease in the  $\eta_{sp}/C_p$ .

The effect of ionic strength on the viscosity was studied by adding various concentrations of salts to the aqueous solutions. The ionic strength was varied by changing the concentration of the added salt. In order to see whether the charge on counterion (cation of the added salt) has any effect on the viscosity, three salts with monovalent, divalent and trivalent cations were added to the solutions. The salts studied were sodium chloride (NaCl), calcium chloride ( $CaCl_2$ ) and aluminium chloride ( $AlCl_3$ ). The salts chosen were such that the anion was common in all of them. It was observed that as the charge on the cation increases, the polymer solution became turbid at very low concentrations of the added salt. For example in case of sodium chloride as added salt, concentrations upto 0.01M could be studied as no precipitation of the polymer occurred. But in case of aluminium chloride, the precipitation occurred at concentrations above  $7 \times 10^{-5}M$  of the added salt. Therefore, only one concentration of this salt could be studied. It was observed that variation in the concentration of the added salt has significant effect on the reduced viscosity. Figure 2 shows a plot of  $\eta_{sp}/C_p$  versus  $C_p$  at various concentrations of the added salt (NaCl). It can be seen from the graphs that increase in ionic strength decreases the reduced viscosity. This decrease in the reduced viscosity is well pronounced in the low  $C_p$  region and becomes poorer as  $C_p$  increases. Also, with increase in ionic strength the maximum shifts

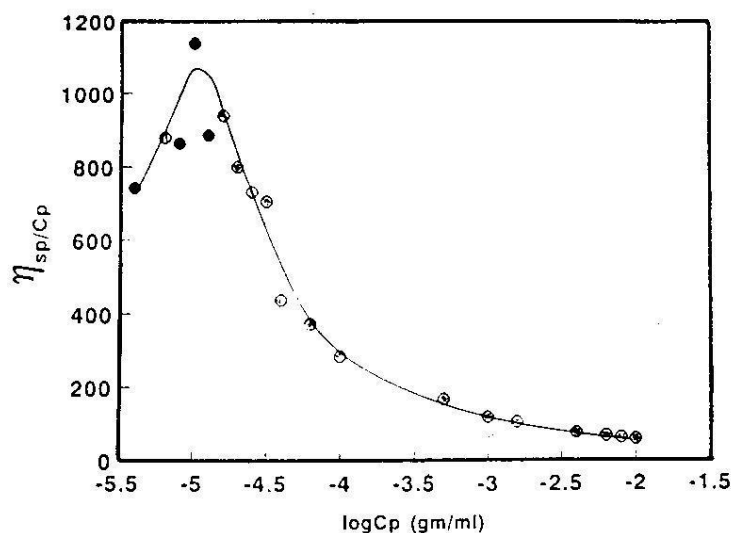


Fig.1: Plot of reduced viscosity versus  $\log C_p$  for various aqueous NaPSS solutions containing no salt at 25°C.

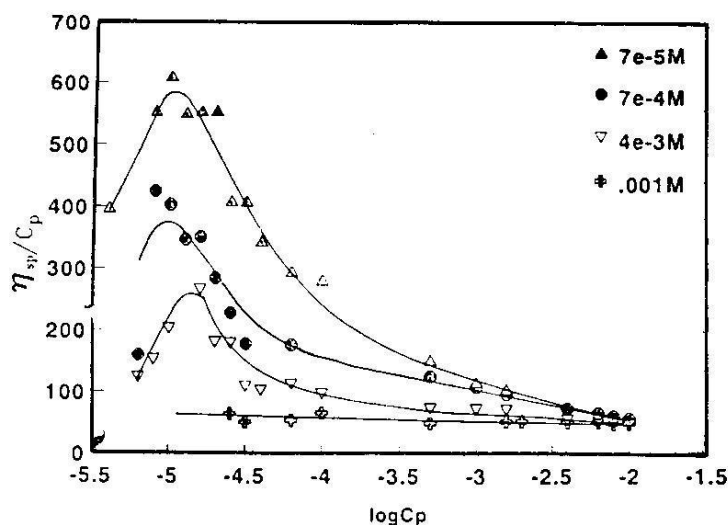


Fig. 2: Plot of reduced viscosity versus  $\log C_p$  for various aq. NaPSS solutions containing different NaCl concentration at 25°C.

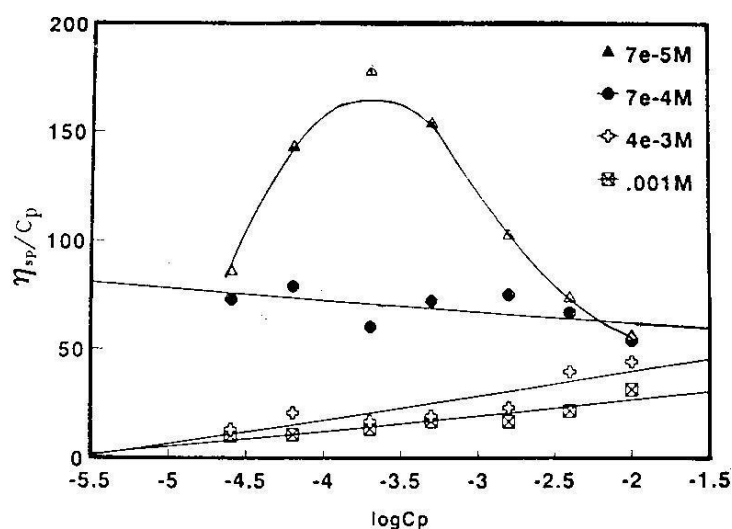


Fig. 3: Plot of reduced viscosity versus  $\log C_p$  for various aq. NaPSS solutions containing different  $\text{CaCl}_2$  concentrations at 25°C.

towards higher polymer concentration, decreases in height and finally disappears. For NaCl, the plot of  $\eta_{sp}/C_p$  vs  $C_p$  becomes linear at 0.01M concentration of the added salt. On further increase in salt concentration, no change in dependence of  $C_p$  occurs and a linear behaviour similar to that of uncharged polymers is observed. This dependence can then be described by the well known Huggins equation.

A similar behaviour was observed when the charge on the cation increase e.g. for  $\text{CaCl}_2$  Figure 3, except that maximum disappeared at relatively lower concentrations of the added salt.

Figure 4 and 5 show a comparison of the effect of valence of the counterion on the reduced viscosity at 25°C. If we compare a single concentration of the three added salt i.e.  $7 \times 10^{-5} \text{M}$ ,

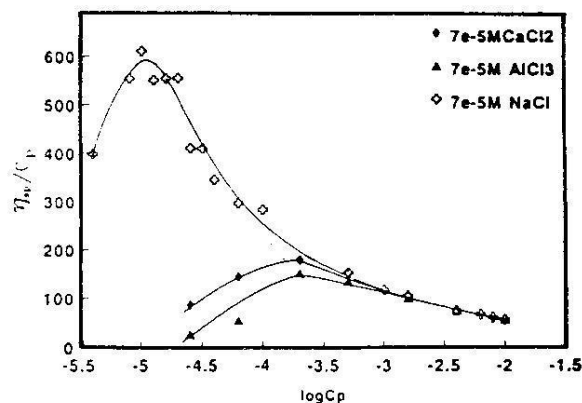


Fig. 4: Plot of reduced viscosity versus  $\log C_p$  for various aq. NaPSS solutions containing different salts at 25°C.

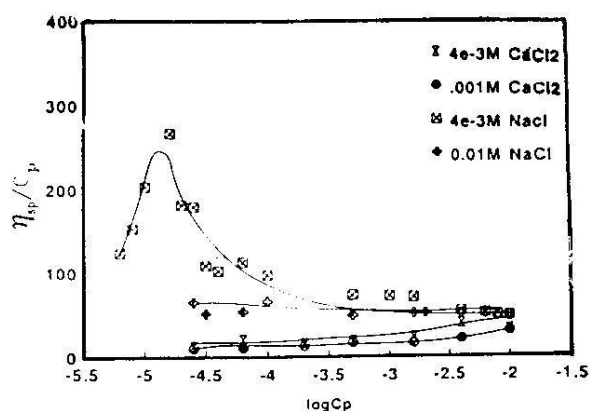


Fig. 5: Plot of reduced viscosity versus  $\log C_p$  for various aq. NaPSS solutions containing different concentrations of NaCl and  $\text{CaCl}_2$  at 25°C.

it can be seen in Figure 4 that the height of the maximum varies in the following order:  $\text{AlCl}_3 > \text{CaCl}_2 > \text{NaCl}$ . Moreover, the maximum is shifted towards higher polymer concentrations for the three salts. A similar behaviour is observed for other concentrations of the mono- and divalent added salts (Figure 5). Figure 6 shows a plot of  $(C_p/C_s)_{\max}$  vs  $I/C_s$ . Where  $C_p$  is the polymer concentration,  $C_s$  is the salt concentration and  $I$  is the ionic strength of the medium. It is evident from the graph that the position of the maximum is shifted to higher  $C_p$  as the charge on the counterion increases.

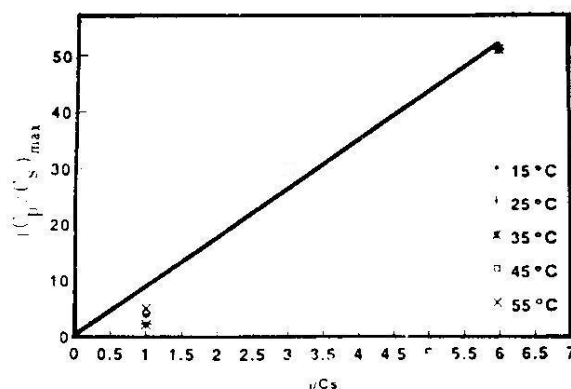


Fig. 6: Plot of  $(C_p/C_s)_{\max}$  versus  $I/C_s$  for aq. NaPSS solutions at different temperatures.

From our observations, we confirm the findings of Cohen *et al.* [2,3] that with dilution the reduced viscosity of polyelectrolyte solutions increases first, passes through a maximum and then decreases. Normal polymer behaviour is recovered in the limit of infinite dilution. This observation is in contradiction to the early findings that reduced viscosity of polyelectrolyte solutions increases infinitely in the limit of zero concentration. The presence of maximum in the  $\eta_{sp}/C_p$  vs  $C_p$  curve in the dilute region can be explained in different ways. For example Cohen *et al.* [1,2,3] explains it in terms of the expansion of polymer coils upon dilution. Expansion of the coils occurs due to enhanced dissociation of the ionizable groups. Thus negative charges of NaPSS repel each other intramolecularly causing expansion of the polymer coil to rod shape from flexible coil shape. During this expansion process, size of the coil increases and therefore  $\eta_{sp}/C_p$  increases. When the coil attains its maximum extension so that on further dilution no expansion occurs, the  $\eta_{sp}/C_p$  decreases, as now dilution provides more free space for the coils to move. However, it is difficult to conclude that the above mentioned mechanism is solely responsible for the observed behaviour in the light of observations made by other workers for other systems. For example a similar observation has been reported by Yamanaka *et al.* [4,5,6] for suspension of polymer latex particles whose size is not expected to change with concentration. Hara *et al.* [7] also reported a similar behaviour for halato telechelic ionomers. These ionomers have only one ionic end group, so

that the intramolecular coulombic interaction does not come into question. In the light of these observations it is difficult to say that intramolecular conformational changes are solely responsible for the observed behaviour. It appears that intermolecular interactions also play an important role in the solution behaviour of polyelectrolytes.

#### Experimental

Poly (sodium-4-styrene sulfonate) (NaPSS),  $M_w = 70,000$ , used in the present investigation was obtained from Aldrich Chemical Company Inc., USA. The salts used were sodium chloride (NaCl), calcium chloride ( $\text{CaCl}_2$ ) and aluminium chloride ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) from Reidel-de-Haen AG, Merck and Aldrich Chemical Companies respectively. Doubly distilled water was used for solution preparation. Stock solutions of higher concentrations were prepared by weighing the required amount of the polymer on Sartorius G.M.B.H. type balance, Germany. All other solutions were prepared by dilution method. Ostwald viscometer No. 3711, type BS/U size A. England, was used to find the flow time of the solvent and solutions with the help of a digital stop watch with an accuracy of 0.01 Sec in a thermostat ( type C-135. Isuzu-Seisa Kushi,

Japan). A digital thermometer (J & L Pt 100, Germany) sensitive to  $0.1^\circ\text{C}$  was also used alongwith a conventional mercury thermometer in order to keep a strict check on temperature variation.

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