DETERMINATION OF THE AVERAGE MOLECULAR WEIGHT OF SODIUM POLYSTYRENESULPHONATE FROM VISCOSITY MEASUREMENT.

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Abstract: Precise measurements on the viscosity of aqueous solutions of sodium polystyrenesulphonate and in presence 0.1 N sodium chloride at 308.15 K were reported. The degree of substitution of sodium polystyrenesulphonate used was one. The sodium polystyrenesulphonate (NaPSS) used in these investigations was purchased from Aldrich Chemical Company, Inc. whose viscosity average molecular weight was 70,000. The experimental viscosity average molecular weight of polystyrenesulphonate was found 70,186.15.

Key Words: Sodium polystyrenesulphonate; Staudinger equation; Intrinsic viscosity; Degree of substitution.

INTRODUCTION

The most distinguishing property of a polymer solution is its viscosity which is different from that of the pure solvent. Staudinger in 1930 suggested that the increase in viscosity on dissolving a polymer in a solvent may be correlated with the molecular weight of the polymer. Since then, developments in the theory and experiments have confirmed the essential basis of Staudinger's suggestion.

Determination of viscosity average molecular weight requires the measurement of the viscosity of a polymer solution relative to that of the solvent. Since only relative measurements are required, capillary viscometers are well suited for this purpose and are frequently used, the most suited viscometers being Ostwald viscometer and a Schultz-Immergut-type viscometer with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. In the later, dilutions of the solution can be carried out and the measurements made at a number of concentrations. The most important application of viscosity in the field of polymer chemistry is in the determination of molecular weights. Although by viscosity measurements alone it is only possible to observe the changes in molecular weight, the absolute value of molecular weight can be determined if suitable calibration of intrinsic viscosity $[\eta]$ versus molecular weight $[M]$ is available for a particular polymer/ solvent system.

The original Staudinger equation relating molecular weight to intrinsic viscosity was replaced by the general relation, $[\eta] = KM_v^{\alpha}$ (1)

This equation is known as Mark-Houwink-Sakurada (M.H.S) equation[1]. Neither the constant K nor the exponent á can be derived theoretically. The experimental method of their evaluation involves the separation of the polymer into several fractions followed by the determination of the intrinsic viscosity and absolute molecular weight of each fraction. Factors that affect the value of include molecular weight, temperature, shear rate, chain stiffness and topology, solvent quality, and polydispersity. The values of constant K and the exponent á are obtained from the intercept and slope of a double logarithmic plot of intrinsic viscosity versus molecular weight. The value of the exponent á lies between 0.6 and 0.8 although values from 0.5 to 1.0 are possible. Further, the values of K and á vary with the solvent and temperature.

The objective of the present research work is to determine the average molecular weight of Sodium polystyrenesulphonate which can be obtained very easily from viscosity measurement.

EXPERIMENTAL

Triply distilled water with a specific conductance less than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the solution. The sodium salt of polystyrenesulfonic acid (NaPSS) employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was 70 kDa with a degree of substitution (DS) of 1.0 and these values agree well with those obtained from physiochemical characterization in this study.

The viscometric measurement was performed at 308.15K using a Schultz-Immergut-type viscometer [2] with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. The measurements were made in a thermostat maintained within 0.05 ^{0}C of the desired temperature by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated

platinum resistance thermometer and Muller bridge[3,4]. Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosities depend on the shear rate in the concentration range investigated; measurements with capillaries of different sizes were performed. This did not lead to different values of the reduced viscosity.

RESULTS AND DISCUSSION

Dilution in salt free solutions or in the presence of varying salt concentrations ($c_s = \sim 1\times10^{-4}$, $\sim 1\times10^{-2}$ and $\sim5\times10^{-1}$ N NaCl) was performed. Figures 1 and 2 show the variation of the reduced viscosity for sodium polystyrenesulphonate as a function of polymer concentration. The concentration and reduced viscosity values for sodium polystyrenesulphonate solution in water is given in Table 1 and the concentration and reduced viscosity values for sodium polystyrenesulphonate solution in (0.1 N NaCl) is given in Table 2. The degree to which the viscosity of a solvent is enhanced by the addition of polymer can be expressed by the specific viscosity η_{sp}, defined by $\eta - \eta_s / \eta_s$, where η and are the solution and solvent viscosities, respectively. The reduced viscosity (η_{sp}/c_p) describes the change in the specific viscosity with polymer concentration c_p. The reduced viscosity data as functions of polymer concentration can be described by the well-known Huggins equation[5,6]

$$\eta_{sp}/c_P = [\eta] + k_H[\eta]^2 c_P \qquad (2)$$

where $[\eta]$ is the intrinsic viscosity describing the solvodynamic behaviour of the polymer molecules in solution, c_p is the polyelectrolyte concentration and k_H is the Huggins constant which is a characteristic for a given polymer-solvent system.

From the present experimental (η_{sp}/c_p) versus c_p data, the intrinsic viscosities and the Huggins constants have been determined by method of least-squares using equation (2).

The intrinsic viscosity describes the contribution an isolated polymer makes to the solution viscosity in the absence of interpolymer interactions. The Huggins coefficient represents specific hydrodynamic interactions of the polymer and solvent. For uncharged polymers k_H typically takes values ranging from 0.4 to 0.76 for a given polymer-solvent system. These two values have been shown by theoretical developments to correspond to the free-draining [7] and non-draining [8] limits, respectively.

The anomalous concentration dependence of viscosity of polyelectrolyte solutions with no added salt has been known for a long period [9]. Early investigations appeared to suggest an unbound rise in the reduced viscosity = specific viscosity and c_p = polymer concentration of salt-free polyelectrolyte solutions as one lowers the polyion concentration [10-11]. In these studies, which are summarized in the pioneering work of Fuoss [10-11], a straight line is obtained when the reciprocal of reduced viscosity is plotted against the square root of the concentration. It was usually assumed that this line could be extrapolated to zero polyelectrolyte

concentration and that the intercept at zero concentration gives the inverse of the intrinsic viscosity. However, careful investigations on the dilute solution behavior revealed that the apparent unbounded rise in the reduced viscosity is always followed by a maximum [12], and normal polymer behavior is recovered at the extrapolated limit of zero polyelectrolyte concentration. Thus the method of Fuoss could not be used to obtain the intrinsic viscosity and, in fact, this is now known to be one of the capital errors in polyelectrolyte history. It has been argued that the observed behavior is a consequence of the screening of long-range intermolecular interactions by the residual electrolytes in the solution [12]. Most of the experimental work dealt with the existence of the maximum that appeared at relatively low polymer concentration and, therefore, was close to the limit of accuracy of the measuring systems. Therefore, it is virtually impossible to obtain the intrinsic viscosity of polyelectrolyte solutions without added salt since the concentrations beneath the viscosity maximum are in the very low

Table 1: Sodium polystyrenesulphonate solution in water.

Concentration (gm.cm^{-3})	Reduced Viscosity (cm^3.gm^{-1})
0.002004	156.74
0.001670	173.61
0.001253	206.17
0.000910	257.71
0.000668	319.29
0.000360	487.28
0.000225	702.30
6.41×10^{-5}	356.68
4.00×10^{-5}	310.37
2.80×10^{-5}	302.24

Table 2: Sodium polystyrenesulphonate solution in salt (0.1 N NaCl).

Concentration (gm.cm^{-3})	Reduced Viscosity (cm^3.gm^{-1})
0.006144	33.03
0.004096	33.31
0.003072	34.46
0.002087	30.90
0.001539	30.60
0.001080	30.29
0.000751	30.05
0.000329	29.73

concentration region difficult to reach experimentally.

Figure 3 shows the variation of the reduced viscosity for sodium polystyrenesulphonate as a function of polymer

concentration of 0.1 N NaCl.

In absence of the added salt, the values increase with dilution and decreases in the dilute region. As the salt concentration increases, the values decreases drastically and a maximum is seen for solution containing ~ 1×10^{-4} N NaCl in water. No maximum is however detected for systems containing ~ 1×10^{-2}, ~ 1×10^{-1} and ~ 5×10^{-1} N NaCl. The values for these two cases (~ 1×10^{-1} and ~ 5×10^{-1} N NaCl) agree very well with those obtained from equation (2) and there was a linear variation of reduced viscosity with concentration of polyelectrolyte. To calculate, molecular weight of Sodium polystyrenesulphonate using M.H.S. Equation, K =1.62´10^{-4} at 308.15K

and á = 0.88 at 308.15K which were taken from[13]. From figure 3, the intercept gives intrinsic viscosity which is =29.8 $cm^3.gm^{-1}$ = 2.98 $dl.gm^{-1}$ and is obtained from the graph between reduced viscosity versus polymer concentration represent in Table 2. By putting the known values, in equation (1), the average molecular weight of polystyrenesulphonate was found to be, M_v = 70186.15.
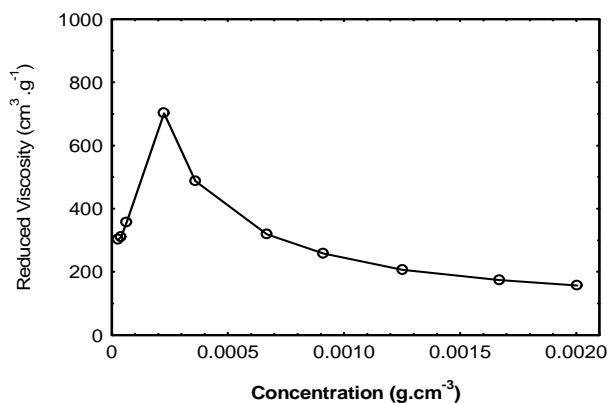

Fig. 1: The variation of the reduced viscosity for sodium polystyrenesulphonate as a function of polyelectrolyte concentration.
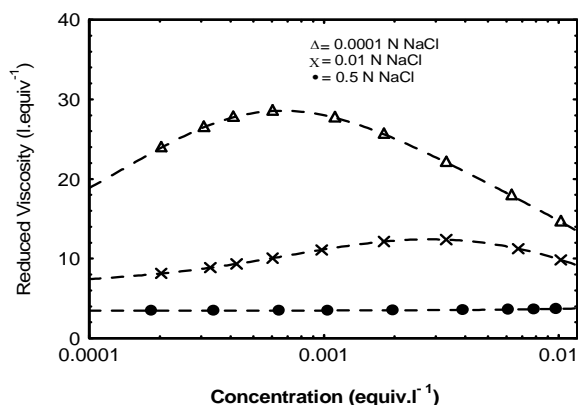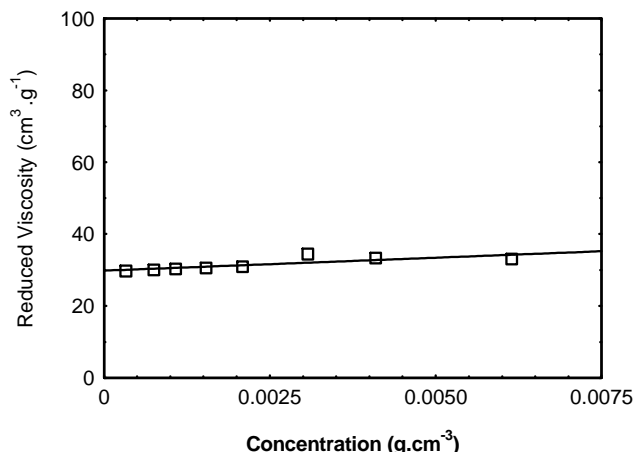

Fig. 2: The variation of the reduced viscosity for sodium polystyrenesulphonate as a function of polyelectrolyte concentration in presence of ~1 x 10^{-4} N NaCl (triangles), in presence of ~1 x 10^{-2} N NaCl (crosses), and in presence of ~5 x 10^{-1} N NaCl (closed circles). The dashed lines represent the fits.

Fig. 3: The variation of the reduced viscosity for sodium polystyrenesulphonate as a function of polyelectrolyte concentration in presence of ~1 x 10^{-1} N NaCl (squares). Lines represent the fits according to equation (2).

CONCLUSIONS

It has been successfully measured the molecular weight of Sodium polystyrenesulphonate in presence of NaCl solution.

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