Viscometric Constants for Sodium Polystyrene Sulfonate Standards in Solvents of 0.1 M CH_3COOH/0.2 M NaCl and 0.2 M CH_3COOH/0.1 M CH_3COONa at 25.0 °C

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The viscometric or Mark−Houwink constants K and a for sodium polystyrene sulfonate (NaPSS) standards in two different aqueous solvents (0.1 M CH_3COOH/0.2 M NaCl and 0.2 M CH_3COOH/0.1 M CH_3COONa) were determined at 25.0 °C using a Ubbelohde viscometer. They are 3.288×10^{-3} mL·g^{-1} and 1.908×10^{-3} mL·g^{-1} for K and 0.788 and 0.851 for a for the above two solvent systems, respectively. These constants were then used for establishing the universal calibration relationship for a size exclusion chromatography column using the above two aqueous solvents as the mobile phase.

Introduction

One of the most characteristic features of a dilute polymer solution is that its viscosity is considerably higher than that of the pure solvent (Allen and Bevington, 1989). This arises because of the large differences in size between polymer and solvent molecules and can be significant even at very low polymer concentrations, especially for polyelectrolytes and polymers with high molecular weights. Dilute solution viscometry is concerned with accurate quantitative measurements of the increase in viscosity and allows determination of the intrinsic ability of a polymer to increase the viscosity of a particular solvent at a given temperature. This quantity provides a wealth of information relating the size of the polymer molecule in solution, including the effects upon the chain dimensions of the polymer structure, the molecular shape, the degree of polymerization, and the polymer−solvent interactions. Most commonly, however, it is used to estimate the molecular weight of a polymer.

The following empirical equation was proposed by several workers and is known by various combinations of their names, though most commonly as the Mark−Houwink equation

$$[\eta] = KM_v^{\,a} \tag{1}$$

where M_v is the viscosity average molecular weight and K and a are constants for a given polymer/solvent/temperature system. Generally, $0.5 \le a \le 0.8$ for flexible chains, $0.8 \le a \le 1.0$ for inherently stiff molecules, and $1.0 \le a \le 1.7$ for highly extended chains such as polyelectrolytes in solutions of very low ionic strength. The values of K tend to decrease as a increases, and for flexible chains it is typically in the range 10^{-3} to 10^{-1} cm^3·g^{-1}. The above equation allows evaluation of M_v from the intrinsic viscosity of a polymer solution $[\eta]$ provided that K and a are known for the system under study. The most widely used method for evaluation of K and a involves measurement of $[\eta]$ for a series of the concerned polymer standards with known M_n (number average molecular weight) or M_w (weight average molecular weight). Generally, a plot of log $[\eta]$ against log M is fitted to a straight line, from which K and a are determined.

Table 1. Characteristics of NaPSS Standards

standard no.	M_w	M_n	M_w/M_n	water content (mass %)
621	16 600	14 700	1.13	11.0
622	34 700	29 900	1.16	9.0
872	57 500	52 100	1.11	9.5
624	127 000	103 200	1.23	10.5
625	262 600	218 400	1.20	12.5

The main purpose of this study is to obtain the Mark−Houwink constants K and a for sodium polystyrene sulfonate (NaPSS) standards in two different aqueous solvent systems: 0.1 M CH_3COOH/0.2 M NaCl and 0.2 M CH_3COOH/0.1 M CH_3COONa, respectively, at 25 °C. The two studied solvent systems are often used in characterization methods, such as size exclusion chromatography (SEC), for polyelectrolytes of natural origin, such as chitosan (Knaul et al., 1998). In such a characterization technique, a universal calibration relationship should be established for the SEC system where the values of the Mark−Houwink constants are essential for both standard and unknown polyelectrolytes (Grubisic et al., 1967). The constants K and a for NaPSS standards in the two studied solvents are not available in the literature.

Experimental Section

Materials. Five samples of sodium polystyrene sulfonate (NaPSS) standards were obtained as HPLC grade from Scientific Polymer Products Inc. Their characteristics are listed in Table 1. Glacial acetic acid, sodium chloride crystals, and sodium acetate crystals were procured as reagent grade from Caledon Laboratories Ltd. and were used as received without further purification.

In the case of NaPSS standards, it is well-known that polyelectrolytes are usually hygroscopic and typically contain about 10% by mass of moisture (Allen and Bevington, 1989). Both moisture and impurities need to be taken into account in determining the weight concentra-

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tions of NaPSS in solutions. The moisture and low-molecular-weight impurities contents of the NaPSS standards, listed also in Table 1, were determined using a Texas Instruments 2050 TGA thermogravimetric analyzer. The sample of about 5 mg was heated from room temperature to 300 °C at 10 °C min^{-1} under a nitrogen atmosphere. The large abrupt weight loss of the sample up to 150 °C was taken to be the result of evaporation of water and other volatile compounds.

Viscosity Measurements. Aqueous solutions of NaPSS standards in two solvent systems, 0.1 M CH_3COOH/0.2 M NaCl and 0.1 M CH_3COOH/0.2 M CH_3COONa, were prepared by mass to an accuracy of ± 0.0001 $\mathrm{g \cdot dL^{-1}}$. The original concentrations of the solutions were up to about 2.0 $\mathrm{g \cdot dL^{-1}}$ and were already corrected for the moisture content in NaPSS standards using the values reported in Table 1. All pure solvents and solutions were filtered to 0.45 μm using a cellulose type filter prior to use.

Viscosities were measured at 25 ± 0.05 °C using a Ubbelohde viscometer, Model Cannon 100 102, which yielded average flow times of 188.78 s and 107.46 s for the two pure solvents, respectively. Flow times were determined using an optoelectronic sensor directly installed at the meniscus of the viscometer, and their uncertainties were ± 0.01 s. For each standard solution, six dilutions with corresponding pure solvent were used, the flow time measurements were repeated three times, and the average values were used to calculate the reduced viscosity for that solution.

Size Exclusion Chromatography (SEC) on NaPSS Standards. Solutions of about 0.1 $\mathrm{g \cdot dL^{-1}}$ of NaPSS standards in the studied solvents were injected into a SEC column, Model Biosep-sec-S4000, made by Phenomenex. The column dimensions were 300 mm × 7.8 mm, and it was made of stainless steel. Pure solvents, previously degassed using helium, were used as the mobile phase. Both the mobile phase and the standard solutions were filtered through a 0.45 μm cellulose filter prior to column injection. The SEC system incorporated a Shimadzu LC-6A series pump, which maintained the liquid flow rate constant at 1.0 $\mathrm{mL \cdot min^{-1}}$ under a pressure of 300 $\mathrm{kg \cdot cm^{-2}}$ with zero attenuation. The system detectors were a Spectroflow 773 UV detector set at 254 nm and sensitivity 0.2, and a Shodex RI-SE-51 refractive index detector set at negative polarity. The temperature of the column was maintained at 25 °C.

Results and Discussion

Viscometric Constants. The flow time data for solutions of each NaPSS standard in a given solvent were used to calculate the relative viscosity, the reduced viscosity, and then the intrinsic viscosity $[\eta]$ by a linear regression of the reduced viscosity versus concentration (Allcock and Lampe, 1990). The correlation coefficients were >0.990 for all NaPSS standard solutions. This satisfying linearity of all data sets is first attributed to a high accuracy of measurements but more importantly to the presence of a suitable amount of single electrolytes, NaCl and CH_3COONa, respectively, in the acetic acid solution. Otherwise, one would expect to observe a large dependence of the reduced viscosity on the concentration, most significantly in the low-concentration range (Manning, 1969). This is typical for a polyelectrolyte whose molecular chains become extended as they progressively lose their charge due to the escape of some counterions from the polymer backbones, leaving the latter oppositely charged. The effect of an extended polymer molecule on the viscosity of the solution is greater than that of a random polymer chain. Consequently, if the polyelectrolyte solutions contain sufficiently large amounts of simple electrolytes, such as the sodium chloride and sodium acetate used in this study, their reduced viscosities are expected to change linearly with concentration, similar to that of an uncharged polymer solution.

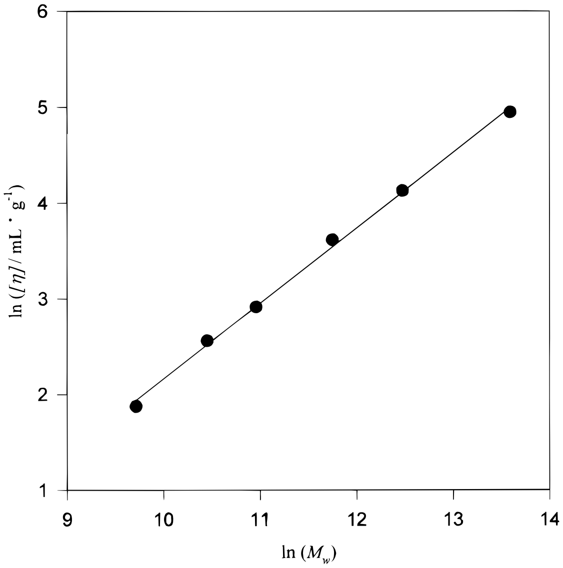

Figure 1. Plot of ln $[\eta]$ versus ln $[M_w]$ for NaPSS standards in 0.1 M CH_3COOH/0.2 M NaCl.

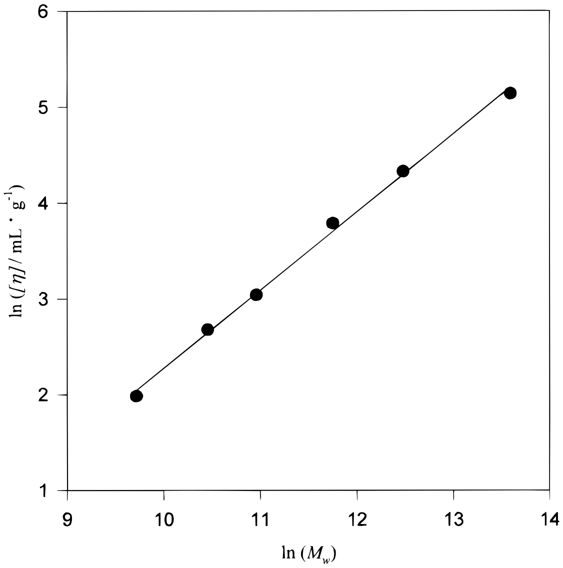

Figure 2. Plot of ln $[\eta]$ versus ln $[M_w]$ for NaPSS standards in 0.2 M CH_3COOH/0.1 M CH_3COONa.

Since the NaPSS samples used in this study are standard ones whose polydispersity indices range between 1.13 and 1.23, their viscosity average molecular weight M_v in eq 1 could be suitably replaced by their corresponding M_w (Table 1). A plot of ln $[\eta]$ versus ln $[M_w]$ is shown in Figures 1 and 2 for the two studied solvent systems, respectively. The deduced Mark−Houwink constants K and a are listed in Table 2 together with the values of the standard errors obtained using the least-squares method. The obtained values of a are slightly different between the two solvent systems; this may be mainly attributed to the effect of the ionic strength of each solvent system on the molecular shape of NaPSS in the corresponding solution. The values of a, slightly smaller than 1.0 but not exceeding 1.0, indicate that the polyelectrolyte molecules behave like

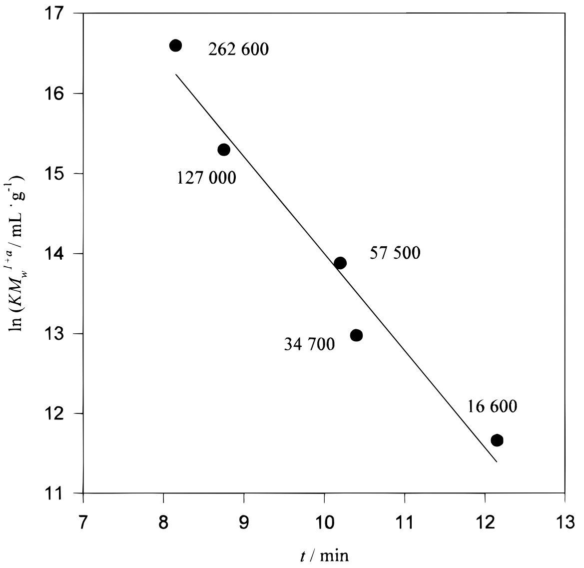

Figure 3. SEC universal calibration relationship for NaPSS standards in 0.1 M CH_3COOH/0.2 M NaCl.

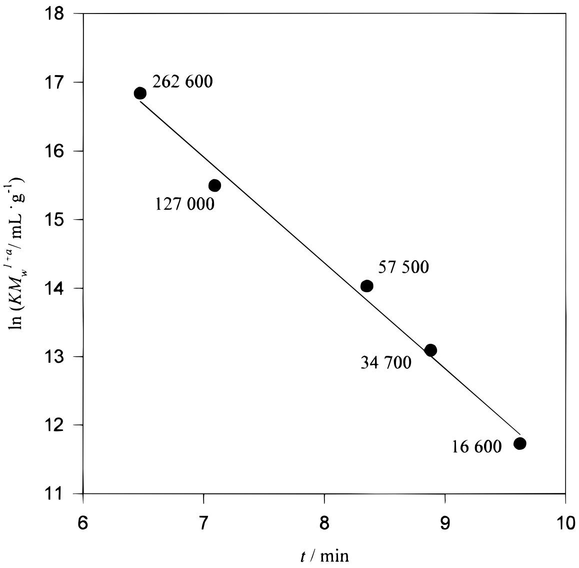

Figure 4. SEC universal calibration relationship for NaPSS standards in 0.2 M CH_3COOH/0.1 M $NaCH_3COO$.

Table 2. Viscometric or Mark−Houwink Constants *K* and *a* for NaPSS Standards, at 25 °C

solvent	10^3K (mL·g^{-1})	*a*	standard error
0.1 M CH_3COOH/0.2 M NaCl	3.288	0.788	0.0578
0.2 M CH_3COOH/0.1 M $NaCH_3COO$	1.908	0.851	0.0663

Table 3. Correlation of the SEC Universal Calibrations

solvent	slope *A* (mL·g^{-1}·min^{-1})	intercept *B* (mL·g^{-1})	standard error
0.1 M HCH_3COO/ 0.2 M NaCl	−0.7944	21.118	0.3457
0.2 M HCH_3COO/ 0.1 M $NaCH_3COO$	−1.5431	26.709	0.2277

inherently stiff ones but not highly extended chains. This is in accordance with the above discussion concerning the effects of a simple electrolyte on the hydrodynamic behavior of the polyelectrolyte. Furthermore, on the basis of the compositions of the two studied solvents, they differ much in pH and ionic strength. Since acetic acid is a weak acid, it is difficult to know the true ionic strength of the solvents. However, on the basis of the salt concentrations, the NaCl solution (0.2 M) has a higher ionic strength than the $NaCH_3COO$ (0.1 M) solution. This explains the lower value of *a* for the NaCl solution: its higher ionic strength leads to better screening of the electrostatic repulsion between the acid groups in the PSS molecule; consequently, the polymer chain is more flexible.

SEC Calibration Relationship. One of the most common uses of NaPSS standards is to establish the universal calibration relationship for a SEC system operating with aqueous solvents in which an unknown polyelectrolyte has to be characterized. In such a universal calibration, the differences in hydrodynamic behaviors between NaPSS standards and the unknown polyelectrolyte can be taken into account by using the product of the weight average molecular weight of each compound and its corresponding intrinsic viscosity, through the use of the Mark−Houwink constants *K* and *a* (Allcock and Lampe, 1990):

$$\ln [\eta]_x M_x = \ln [\eta]_s M_s \tag{2}$$

or

$$\ln K_x M_x^{ax+1} = \ln K_s M_s^{as+1} \tag{3}$$

where the subscript *x* represents the unknown compound and *s* represents the standard polymer.

Figures 3 and 4 represent the SEC universal calibration curves for NaPSS standards in the two solvent systems studied, respectively. It is found that both universal calibration relationships are fairly linear over the relatively large molecular weight range of the standard samples used. The regression coefficients are >0.990, with the main uncertainties attributed to those of the retention times of the samples, which were partly linked to some extent of polydispersity of the standards used. To make the calibration curves more useful when applied to an unknown polyelectrolyte sample, the data from Figures 3 and 4 are correlated using a linear expression:

$$y = At + B \tag{4}$$

where *t* represents the elution time and *y* represents the term $\ln [KM^{a+1}]$. The values of the slope *A* and the intercept *B* together with those of the standard errors are reported in Table 3 for both solvent systems, respectively. When applying the above universal calibration curves to SEC measurements performed under similar conditions for an unknown polymer sample, the experimental value of the retention time will be substituted into eq 4 to yield the value of the term $\ln [K_x M^{ax+1}]$, which then gives rise to the value of its molecular mass if the values of the Mark−Houwink constants for the unknown polymer in the given solvent K_x and a_x are known.

Conclusion

The viscometric or Mark−Houwink constants *K* and *a* were accurately obtained for sodium sulfonated polystyrene standards in two different aqueous solvent systems: 0.1 M CH_3COOH/0.2 M NaCl and 0.2 M CH_3COOH/0.1 M $NaCH_3COO$. Due to the presence of simple electrolytes, NaCl and $NaCH_3COO$, respectively, of sufficiently large concentrations in the two studied solvent systems, the reduced viscosities of solutions of NaPSS standards changed quite linearly with the concentration. The values of the constant *a* indicated that NaPSS molecules behave like stiff chains which, however, are not extended substantially in those two solvent systems; also, its lower value for the first solvent system with respect to the second one is likely caused by the stronger ionic strength of the former. Finally, the obtained viscometric constants were successfully applied for establishing a universal calibration relationship of a size exclusion chromatography system using the above solvent systems, respectively, as the mobile phase.

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