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Short Communication

Temperature Dependence of the Diffusion Coefficients and Effective Charge Numbers of Polystyrenesulfonate. A Comparison with Lignosulfonate

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In our previous works[1,2] the effective charge number of lignosulfonate was measured as a function of temperature. The fraction of efficiently dissociated charges was found to be about 30% in the temperature range 10–30°C, but at 40°C it suddenly dropped to zero. The measurements were carried out in different salt solutions (NaCl, LiCl, KF) and with different ionic strengths (0.01–1.0 M). In all of these measurements the conformation of the lignosulfonate macromolecule seemed to be a compact sphere. (The molecular weight exponent of the Mark–Houwink relation was ca. 0.3.) However, when the measurements were carried out under a weak external electric field (10–35 V m^{-1}) the conformation was changed to be a non-free-draining coil (Mark–Houwink exponent 0.6), but the charge number did not go to zero at 20 or 40°C.[3] Furthermore, the effective charge number was also measured for cytochrome c, which is a globular protein, and the result was the same as for lignosulfonate: the effective charge number was zero at 40°C.[4]

The purpose of the present work is to extend the study described above to include a polyelectrolyte the conformation of which is known to be a linear, random coil, i.e. polystyrenesulfonate. We wish to show that a zero charge number is not obtained with molecules which have the conformation of a linear random coil.

The measurements were carried out by using a method based on a convective diffusion process through a porous membrane. The method has been described earlier.[5–7]

Experimental

Materials. The polydisperse sample of sodium polystyrenesulfonate (NaPSS) was obtained by mixing four standard PSS samples of known molecular weight: M_w = 100000, 35000, 18000 and 5400 g mol^{-1}; $M_w/M_n < 1.1$ and the degree of substitution was 1 for each standard (American Polymer Standards Corp.).

NaCl used as a supporting electrolyte and KCl used as an internal standard were of analytical grade.

The porous membrane was Millipore BD, the pore size was 0.65 μm, and the thickness was 0.15 mm.

Analysis. The concentration of polystyrenesulfonate was determined by UV spectrophotometry at λ = 254 nm. The concentrations of Na^+ and K^+ ions were analysed by AAS. The molecular weight distribution of PSS samples was determined by gel chromatography as described previously.[5]

Measurements. The measurements were carried out in supporting electrolyte (NaCl) concentrations of 0.1 and 1.0 mol dm^{-3}. The concentration of NaPSS in all of the experiments was 1 g dm^{-3}. The flow rates were adjusted so that the concentration difference of the supporting electrolyte across the membrane was not more than 20%. The flow rates were measured by weighing, and the membrane constant was determined using K^+ ion as an internal standard as described earlier.[5] The temperatures used were 20 ± 0.1, 40 ± 0.1 and 48 ± 0.1 °C when the ionic strength was 0.1 M and 20 ± 0.1 and 40 ± 0.1 °C when the ionic strength was 1.0 M.

Results

Diffusion coefficient and chain conformation. The diffusion coefficients and the Mark–Houwink exponents of NaPSS are presented in Table 1, and the molecular weight dependences of the diffusion coefficients in two different ionic conditions at the temperatures of 20, 40 and 48°C are shown in Figs. 1 and 2. The Mark–Houwink exponent increases a little with increasing temperature, indicating a slight loosening of the coil. On the other hand, the increase in ionic strength decreases the expo-

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Table 1. Diffusion coefficients D (in 10^{-6} $cm^2 s^{-1}$) and Mark–Houwink exponents (b) of NaPSS.

	$C_{NaCl} = 0.1$ mol dm^{-3}		
M/g mol^{-1}	$T = 20$°C	$T = 40$°C	$T = 48$°C
100000	0.38	0.51	0.59
35000	0.66	0.89	1.09
18000	1.01	1.38	1.66
5400	2.05	2.93	3.46
$-b$	0.58	0.60	0.61

	$C_{NaCl} = 1.0$ mol dm^{-3}	
M/g mol^{-1}	$T = 20$°C	$T = 40$°C
100000	0.58	0.69
35000	0.98	1.23
18000	1.37	1.77
5400	2.79	3.57
$-b$	0.54	0.56

nent, which means that the conformation of the macromolecule becomes more compact in concentrated salt solutions. This result is in agreement with the results of Wang and Yu.[8] However, it is evident that the conformation of NaPSS remains as a random coil under the conditions studied, i.e. the Mark–Houwink exponent is 0.5–0.6.

The effective charge number. The fraction of effectively dissociated charges (α) of NaPSS as a function of molar mass is shown in Figs. 3 and 4. In order to compare the results with those obtained earlier for sodium lignosulfonate (NaLS)[1,2] we have included the α-values of NaLS in the same figure. In both 0.1 and 1.0 M solutions at 20°C the degree of dissociation of NaPSS is smaller than that of NaLS, which is probably caused by the smaller stoichiometric charge density of NaLS (one sulfonate group in every second monomer unit). There is

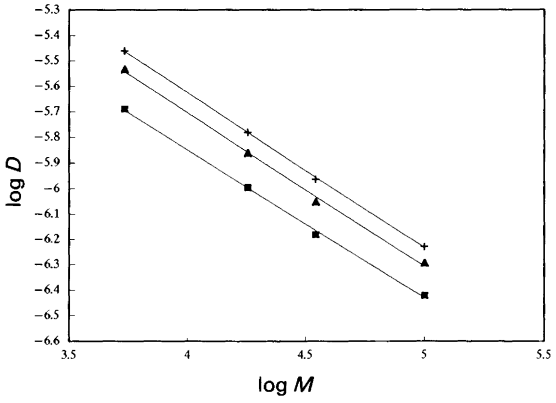

Fig. 1. The diffusion coefficients, D/cm^2 s^{-1}, of NaPSS as a function of the molar mass, M/g mol^{-1}, in 0.1 M NaCl solution. t = ■, 20; ▲, 40 and +, 48°C.

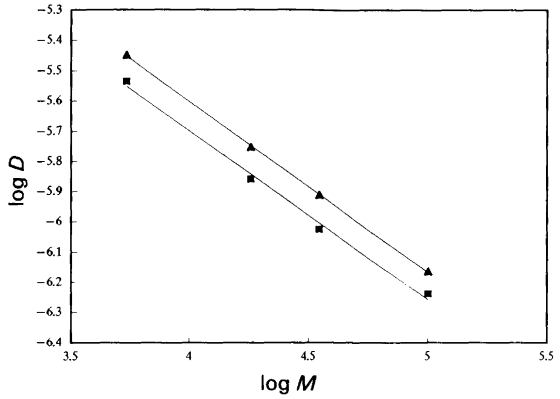

Fig. 2. The diffusion coefficients, D/cm^2 s^{-1}, of NaPSS as a function of the molar mass, M/g mol^{-1}, in 1.0 M NaCl solution. t = ■, 20 and ▲, 40°C.

also a clear difference in the molecular weight dependence of the degree of dissociation: α increases with decreasing molar mass more steeply with NaLS than with NaPSS. At 40°C the difference is more remarkable: when the effective charge number of NaLS is completely zero, for NaPSS it is only a little smaller than its charge number at 20°C.

There are two important differences between PSS and LS macromolecules: (1) the stoichiometric charge density and (2) the conformation. The higher stoichiometric charge density of PSS should increase the ion binding effect compared to that of LS. This means that the effective charge number of PSS should be smaller than that of LS, which is the case at 20°C but not at 40°C. A zero charge number at 40°C has been obtained for lignosulfonate and cytochrome c, which are both compact globular macromolecules.[4] On the other hand, the charge number is not zero at 40°C either for PSS, the conformation of which is a random coil, or for LS the conformation of which has been changed to a loose coil by an external electric field.[3] Thus we conclude that the conformation of the polyelectrolyte has an effect on the complete ion binding at 40°C.

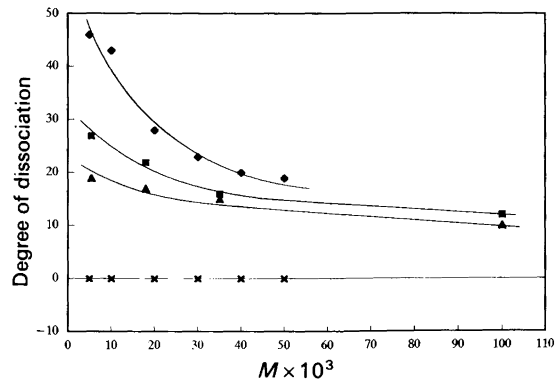

Fig. 3. The degree of efficiently dissociated charges of NaPSS and NaLS as a function of molar mass, M/g mol^{-1}, in 0.1 M NaCl solution. ■, NaPSS (20°C); ◆, NaLS (20°C); ▲, NaPSS (40°C); X, NaLS (40°C).

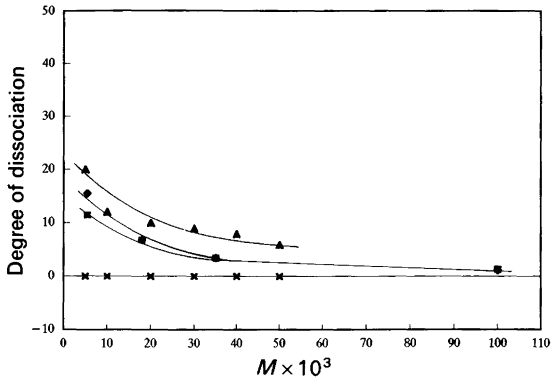

Fig. 4. The degree of efficiently dissociated charges of NaPSS and NaLS as a function of molar mass, M/g mol^{-1}, in 1.0 M NaCl solution. ■, NaPSS (20°C); ◆, NaPSS (40°C); ▲, NaLS (20°C); X, NaLS (40°C).

References

1. Kontturi, A.-K. *J. Chem. Soc., Faraday Trans. 1, 84* (1988) 4043.
2. Kontturi, A.-K., Kontturi, K., Niinikoski, P. and Murtomäki, L. *Acta Chem. Scand. 46* (1992) 941.
3. Kontturi, A.-K., Kontturi, K. and Niinikoski, P. *J. Chem. Soc., Faraday Trans. 87* (1991) 1779.
4. Kontturi, A.-K., Kontturi, K., Niinikoski, P., Savonen, A. and Vuoristo, M. *Acta Chem. Scand. 46* (1992) 348.
5. Kontturi, A.-K. and Kontturi, K. *J. Colloid Interface Sci. 120* (1987) 256.
6. Kontturi, A.-K. and Kontturi, K. *Acta Polytechn. Scand. 178* (1987) 143.
7. Kontturi, A.-K. and Kontturi, K. *J. Colloid Interface Sci. 124* (1988) 328.
8. Wang, L. and Yu, H. *Macromolecules 21* (1988) 3498.

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