Polymer Bulletin 9, 33–39 (1983)

Polymer Bulletin

Electrical Transport in Polystyrenesulfonate Solutions

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Summary

Electric conductance and transport numbers of polyions were measured in aqueous polystyrenesulfonate solutions having different counterions, at concentrations from 2×10^{-3} to $\sim 10^{-1}$ basemol dm^{-3}. From experimental data the extent of atmospheric binding of small ions to polyions was derived. The resulting fraction of free counterions was found to agree within $\pm5\%$ with the coefficient of self diffusion calculated according to the theory of Jackson, Lifson, and Coriell. The molar conductance and the effective charge of the polyion were applied for the calculation of the hydrodynamic friction coefficient related to a monomer unit of the polyion.

Introduction

The electrical transport in polyelectrolyte solutions is mainly governed by the complex electrostatic interactions among all charged particles in the solution. Since an exact theory of the ionic migration in polyelectrolyte systems does not exist at present, the experimental results are often interpreted in terms of a simple concept of ion binding (HUIZENGA et al., 1950; ARMSTRONG and STRAUSS, 1969; KATCHALSKY, 1971). In this work the experimental results will be presented for the conductivity and transport numbers of polystyrenesulfonate solutions having various counterions. It will be shown that the extent of counterion binding derived from experimental data is consistent with the values of the self diffusion coefficient of counterions predicted by the theory of self diffusion (LIFSON and JACKSON, 1962; JACKSON and CORIELL, 1963) applied to the cell model of polyelectrolyte solutions (KATCHALSKY, 1971). In addition, the hydrodynamic friction coefficient of the polyion will be calculated from the experimental data by two entirely different methods giving essentially the same result. The interesting concentration depen-

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dence of this coefficient will be interpreted in a qualitative way.

Experimental

The solutions of polystyrenesulfonic acid (poly-|1-(sulfophenyl) ethylene|), HPSS, and its lithium and potassium salt, LiPSS and KPSS, were prepared from sodium polystyrenesulfonate, NaPSS, with nominal molecular weight of about 4×10^{4}, supplied by Dow Chemical co., Midland, Michigan. The sample was purified by dialysis (ŠPAN and GAČEŠA, 1974) and converted to the acid or corresponding salt by ion exchange.

The polyion constituent transport number was determined by the indirect moving boundary method, and the conductance was measured by the Campbell-Shackleton conductance bridge. Both methods and apparatus have been described in detail in previous papers (ŠPAN and GAČEŠA, 1974; DOLAR et al., 1968, 1974). The measurements were carried out at $25.00 \pm 0.01^{\circ}C$ and within the concentration range 2×10^{-3} - 10^{-1} basemol dm^{-3}. The average accuracy was about ±1% for transport numbers and ±0.5% for molar conductivities.

Results and Duscussion

The concentration dependence of the molar conductivity, λ, and transport number of the polyion constituent, T^{-}, are presented in Figures 1 and 2. For a better comparison, the interpolated results obtained with NaPSS in previous works (ŠPAN and GAČEŠA, 1974; DOLAR et al., 1974) are also included. The influence of the concentration c on these quantities is similar to that observed in previous studies of HPSS (DOLAR et al., 1968) and NaPSS solutions. High values of the polyion constituent transport number indicate that a large fraction of counterions is trapped in the strong electrostatic field around the polyions and thus migrate in the same direction as polyions. Although it is known that the counterions in polysulfonate solutions are not bound to the polyions in a chemical sense (ARMSTRONG and STRAUSS, 1969), it is convenient to classify them into apparently bound and free (HUIZENGA et al., 1950; DARSKUS et al., 1966; KATCHALSKY, 1971). According to these authors the fraction of apparently free counterions, a, may be evaluated from the equation

$$a = \frac{\lambda}{\lambda_{-}+\lambda_{+}} = \frac{\lambda}{T^{-}\lambda+\lambda_{+}(ac)} \qquad (1)$$

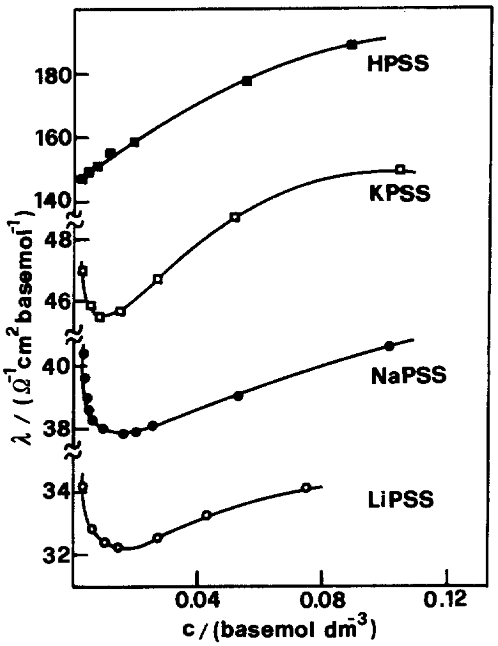

Figure 1. The concentration dependence of the molar conductivity in different polystyrenesulfonate solutions

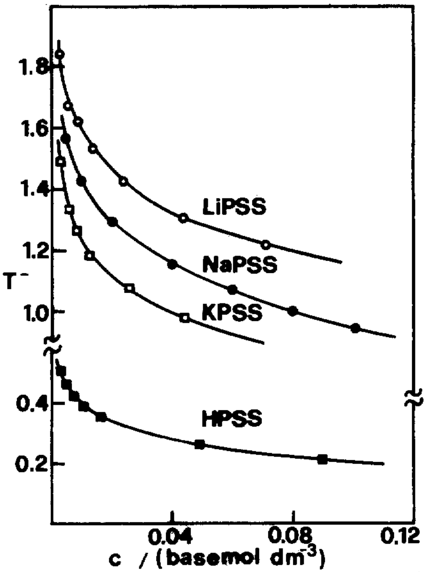

Figure 2. The concentration dependence of the polyion constituent transport number in different polystyrenesulfonate solutions

where $\lambda_-=T^-\lambda$ is the basemolar conductivity of the polyion constituent, and λ_+ is the molar conductivity of the free counterion, which may be, to a good approximation, replaced by the corresponding value for the same ion in the uni-univalent electrolyte at concentration equal to that of free ions, αc (DARSKUS et al., 1966). In this work the Onsager Falkenhagen expression (KORYTA et al., 1970) for $\lambda_+(\alpha c)$ in chloride solution was inserted into equation (1), which was then solved by iteration. The resulting values of α are shown in Figure 3. It is interesting to point out, that the fraction of free counterions, obtained in this way from conductivity and transport numbers, is in a very good agreement with the coefficient of self diffusion of counterions, D_+/D_+^0, predicted by the equation (LIFSON and JACKSON, 1962; JACKSON and CORIELL, 1963)

$$\frac{D_+}{D_+^0} = \frac{1}{\langle\exp(y)\rangle\langle\exp(-y)\rangle} \qquad (2)$$

where the brackets denote the volume average, and $y=-e_0\psi/kT$ is the reduced potential calculated from the solution of the Poisson-Boltzmann equation for the cylindrical cell model

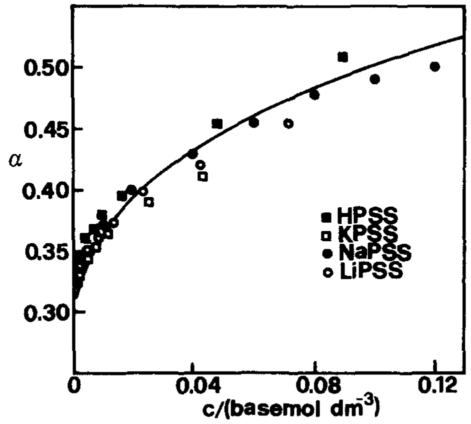

Figure 3. The concentration dependence of the fraction of free counterions in different polystyrenesulfonate solutions: values obtained from experimental data by equation (1) (■ , □ , ● , ○), and theoretical coefficients of self diffusion obtained by equation (2) (solid curve)

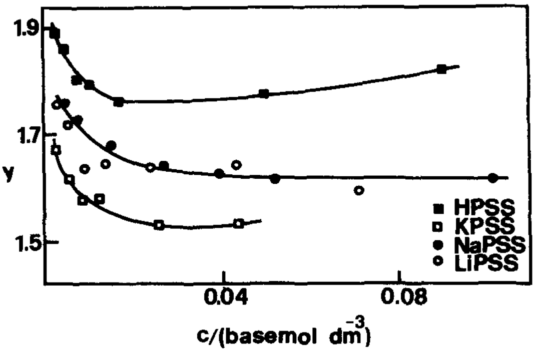

Figure 4. The reduced potential, y(d), at the cylindrical surface around the polyion dividing the counterions into bound and free

of polyelectrolyte solutions (KATCHALSKY, 1971). The coefficients D_+/D_+^0, represented by the solid curve in Figure 3, were calculated by using the structural values of the characteristic parameters of the model for the aqueous solutions of polystyrenesulfonates at 25°C, i.e. the polyion radius a=0.8 nm, the monomer unit length b=0.252 nm, and the relative permittivity ε_r=78.5 (DOLAR, 1974). According to the cell model and the concept of classification of counterions into two groups one can imagine a cylindrical surface surrounding the polyion and dividing the counterions into bound and free. In a previous article (DOLAR et al., 1974) we have calculated the distance d from the polyion axis to this surface and the electrostatic potential, ψ, in this place. The calculation is based on experimental data for the fraction of free counterions (equation 1) and the cylindrical cell model (KATCHALSKY, 1971) with the characteristic parameters given above. It is interesting to note that the value of the reduced potential at this surface, y(d), is almost constant for each species of counterions over a broad concentration range as shown in Figure 4. A small increase at low concentrations does not exceed 10% of the average value. The interpretation of this finding has been given elsewhere (DOLAR et al., 1974).

Considering that the charge of the polyion is partly screened by the atmospherically bound counterions, the force of the external electric field per monomer unit is supposed to be reduced to the fraction α of its value in absence of counterions (KATCHALSKY, 1971). According to this assumption, the hydrodynamic friction coefficient per mole of monomer units, f_{mw}, may be obtained from the relation

$$f_{mw}=\alpha F^2/\lambda_-=1/u_- \qquad (3)$$

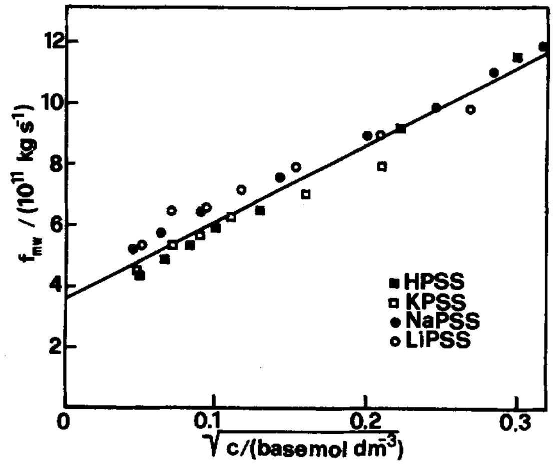

Figure 5. The hydrodynamic friction coefficient per mole of monomer units of the polyion as a function of the square root of concentration

where F is the Faraday constant, and $u_-=1/f_{mw}$ is the absolute mobility, defined as velocity per unit force. The values of f_{mw}, calculated according to equation (3) from experimental data, are presented in Figure 5. A practically linear dependence of f_{mw} on the square root of the concentration is observed, which may be described by the equation:

$$f_{mw}=f^{\infty}_{mw} + k\, c^{1/2}, \quad \text{with} \quad f^{\infty}_{mw}=3.6\times10^{11}\,\text{kg s}^{-1}$$
$$\text{and} \quad k=2.55\times10^{12}\ \text{kg s}^{-1}\ \text{basemol}^{-1/2}\text{dm}^{3/2} \qquad (4)$$

According to the alternative interpretation of experimental data, based on the application of the transformed phenomenological equations of irreversible thermodynamics (SCHMITT and VAROQUI, 1973), T^- is given by

$$T^- = f_{1w}/(f_{mw}+\alpha f_{1w}) \qquad (5)$$

where f_{1w} is the molar hydrodynamic friction coefficient of the counterions, and $(1-\alpha)$ is the fraction of counterions migrating with polyions. If we assume that α and f_{mw} do not depend on the choice of the counterions at given concentration, f_{mw} may be calculated from measured transport numbers T^- of two different polysalts at the same concentration. The friction coefficients f_{mw}, obtained in this way from transport numbers presented in Figure 2, agree on average with those predicted by equation (4) within ±10% in the whole concentration range.

The value of f_{mw} at infinite dilution, f^{∞}_{mw}, determined by either of the two methods, is comparable with that, evaluated from the theoretical expression of RISEMAN and KIRKWOOD (1956), $f^{\infty}_{mw} = f_m / \ln DP$, where $f_m = 3N_A \pi \eta b$ is the molar friction coefficient of an isolated monomer (SCHMITT and VAROQUI, 1973), N_A is the Avogadro constant, η is the viscosity of water, and DP is the degree of polymerization. In our case, $\eta = 9\times10^{-4}$kg m^{-1}s^{-1} and DP=2×10^{2}, equation of RISEMAN and KIRKWOOD (1956) yields the value $f^{\infty}_{mw} = 2.5\times10^{11}$kg s^{-1}.

It is difficult, however, to explain the decrease in the absolute mobility of the chainlike polyion with increasing concentration, though such a behavior would be expected in case of rigid spherical polyions (ARMSTRONG and STRAUSS, 1969). Further, the effect can only to a minor extent be attributed to the conformational changes, since previous studies support the assumption that the PSS polyion behaves likely as a free draining coil with the chain surrounded by a cylindrical ionic atmosphere (NAGASAWA et al., 1972; DOLAR et al., 1974). A part of the atmosphere containing the fraction ($1-\alpha$) of the counterions, together with a certain amount of the solvent enclosed within a cylindrical shear plane (O'BRIEN and WHITE, 1978), is supposed to migrate together with the polyion. One may speculate that, at higher concentrations, this gives rise to a counterflow of the remaining solvent which would increase the hydrodynamic friction. Since the friction coefficient f_{mw} presented in Figure 5 was calculated assuming that the solvent flow is negligible, it is not surprising that its apparent value increases with concentration.

Before concluding, let us mention briefly that recent measurements of conductance and transport numbers in polyethylenesulfonic acid solutions (BRATKO et al., 1978) show that the concentration dependence of the hydrodynamic friction coefficient of polyethylenesulfonate polyion is similar to that observed for PSS polyion in this work.

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Received after revision October 9, accepted November 8, 1982