AQUEOUS SOLUTIONS OF POLYELECTROLYTES

M. Mandel

Department of Physical Chemistry
Gorlaeus Laboratories
University of Leiden
2300 RA Leiden
Netherlands

Polyelectrolytes are macromolecules which, in a suitable polar solvent, usually water, carry a large number of ionized or ionizable groups, often one per monomer unit. Under well defined conditions the macromolecules will bear a considerable charge distributed along the chain (the 'fixed charges') accompanied by an equivalent number of small ions of opposite sign (the 'counterions') in solution. The charge-bearing groups may all be identical or not, but we shall here treat only homopolyelectrolytes, or polyelectrolytes behaving as such. Polyelectrolytes can be of natural origin (nucleic acids, many polysaccharides, etc.) or synthetically prepared (e.g. polyacrylic acid, polyvinyl pyridinium bromide, poly(maleic acid-vinylethylether)-copolymer, etc.).

Aqueous solutions of polyelectrolytes have been shown to exhibit certain specific properties, particularly in the absence of a large excess of simple (low molar mass) electrolyte. The problems arising in the quantitative understanding of these specific effects are, however, very difficult, as they find their origin in a non-additive combination of macromolecular and electrolyte behaviour. Theoretical approaches mainly apply to highly simplified models. From an experimental point of view, polyelectrolyte solutions are often more difficult to handle than either solutions of ordinary macromolecules or of ordinary electrolytes, and proper care must be given to the appropriate experimental conditions necessary to determine certain characteristic quantities for those systems. For instance, the molar mass can only be obtained from classical Rayleigh light-scattering measurements, provided the polyelectrolyte solution...
contains a sufficiently large excess of low molar mass electrolyte, and the refractive index increment of the macromolecule has been determined from measurements on a series of solutions of different macromolecular concentration \( C_M \), in which both water and the low molar mass electrolyte have constant chemical potential \(^{16}\).

1. THE PHENOMENOLOGICAL APPROACH

It is easy to understand qualitatively that the accumulation of identical charges on a macromolecular chain may have a far reaching influence on the average conformation of the polyelectrolyte or the properties derived from it. The electrostatic repulsions between the fixed charges on the same macromolecule will increase the local stiffness of the chain (short-range interactions) and the excluded-volume effect (long-range interactions), both tending to increase the average shape of the macromolecule as compared to a charge-free polymer. These repulsive interactions may be partially screened off by the presence of small ions and by interactions between the polions themselves. It is thus expected that, in a very dilute polyelectrolyte solution, increase of the linear charge density

\[
|\beta| = \frac{Zq}{L}
\]

( where \( Z \) = number of elementary charges, \( q \), fixed on a chain with contour-length, \( L \))

will generally be accompanied by an increase of the average dimensions of the macromolecule, which will tend to become rodlike in the limit of infinite dilution and absence of low molar mass electrolyte. When the concentration of the latter \( C_s \) is increased, this charge effect will be opposed, and additional screening may appear at higher polymer concentrations where the chains have a tendency to become intertwined. Unfortunately, there is no simple experimental means to demonstrate directly the charge- and concentration effects in polyelectrolyte solutions at low \( C_s \). The classic way of measuring radii of gyration of macromolecules (Rayleigh scattering) is not applicable under these conditions. However, this light scattering technique can be applied when there is an excess of 1-1 electrolyte \(( C_s \gg ZC_M)\) and both the charge effect and the salt effect on the dimensions of the polion can be demonstrated \(^2\) (Figure 1). When the salt content is rather low, the change in the average dimensions with increasing charge density can be shown indirectly through a viscometric titration experiment with a weak poly-acid; at constant \( C_m \) and \( C_s \) the reduced viscosity \( \eta_{\text{red}} \equiv (\eta - \eta_o)/\eta_oC_M \) (where \( \eta \) and \( \eta_o \) are the viscosity