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POLYELECTROLYTES, THIRTY YEARS LATER *

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This contribution contains a personal account of the early days of polyelectrolyte research, a discussion of the configurational properties of polyelectrolyte chains, a brief review of polyelectrolyte theories and some remarks concerning recent experimental and theoretical developments as well as future trends.

1. Introduction

Polyelectrolytes, in the words of Fuoss [1] are "substances of high molecular weight which are simultaneously electrolytes". In the modern sense a restriction is made to substances of well defined structure and size, macromolecules existing by virtue of atoms connected by bona fide chemical bonds. This restriction thus excludes colloids, a major component of our environment, Ostwald's famous world of neglected dimensions [2]. Though different in their chemistry from the synthetic and the biological polyelectrolytes, the thermodynamics and the electro-chemistry of the inorganic colloid suspensions are hardly different from those of the former, as can be easily appreciated by reference for instance to the extensive collection of articles edited by Kruyt [3], or by perusal of the study of Verwey and Overbeek [4] on the stability of lyophobic colloids. The physical chemistry of another class of polyelectrolytes, the proteins, was certainly not entirely new at the middle of this century. I hold in my hands the English edition of a little book by Wolfgang Pauli [5] on the colloid chemistry of the proteins, developed according to the author's preface, "from lectures delivered in Vienna — in the winter term of 1912–13. It by no means exhausts the material of the colloid chemistry of the proteins even up to that date". The structure of proteins was hardly understood in those days, but the physical studies revolved around stability, hydration, electric charge (and connection between these), amphoteric electrolytes, dissociation constants, viscosity measurements, isoelectric point (by Sörensen's method), optical rotation, electrical conductivity, properties of the polypeptide linkage, and so on. In 1924, Linderstrøm-Lang [6], hard on the heels of the Debye–Hückel interionic interaction theory of simple electrolytes [7], applied the latter to the potentiometric titration behavior of solutions of proteins. Cohn and Edsall [8] in 1943 summarized the state of knowledge at that time of proteins, amino acids and peptides in their well known monograph.

In many quarters the macromolecular nature of natural and synthetic polymers was not accepted until late into the third decade of our century, following investigations of Staudinger in the twenties. Even Emil Fischer did not accept (cf. Flory [9]) the now commonplace idea that proteins, sugars, cellulose and starches are composed of hundreds and thousands of identical or dissimilar building blocks connected by chemical bonds and not colloidal aggregates of small repeating units. Staudinger, in the grand scheme of his investigations, foresaw the modern study of coiling synthetic polyelectrolytes, first synthesized [10] a typical polyelectrolyte, polyacrylic acid, and in 1938 we encounter [11] an early physico-chemical study by his pupil, Kern, on the osmotic coefficient of

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* Dedicated to the memory of Aharon Katzir-Katchalsky, who was murdered five years ago on May 30, 1972, at Lod Airport.

solutions of this material. Historical and eyewitness aspects of the emergence of the macromolecule concept in the twenties are found in the recent book [12] by Olby on the history of the DNA double helix.

In Jerusalem, Aharon Katchalsky, biologist by training and conviction, gifted with a penetrating physical intuition, and imbued with the realization that a precise understanding of macromolecular structure and function was one of the keys to unlock the riddle of biology, had become aware of the pioneering studies of Werner Kuhn. In 1946, he went to the master in Basel, to extend the theory of statistically coiled macromolecules to the charge-carrying polyelectrolyte systems [13].

My personal involvement with polyelectrolytes began in 1946. Back in Jerusalem from service in World War II, I was guided by my colleague Pnina Spitnik towards doing my thesis work with the young instructor, Aharon, who was bristling with research plans for the future. On a piece of paper he outlined a plan for polyelectrolyte research, parts of which still await execution to-day. I remember well that one of my first activities in polyelectrolytes, cut-off late in 1947 on the Mount Scopus campus, was to correct the proof of the study by Katchalsky and Spitnik [14] of the potentiometric titration of polymethacrylic acid. Later in 1948 we descended to Rehovot, where Aharon founded his school which was to flourish so quickly. Rehovot is not far from Yavneh where another school was founded some two millenia ago by Yohanan bar Zakkai.

We continued to work (in addition to other topical activities) for a while on solutions of polymethacrylic acid, about which another nostalgic story can be told. Polymethacrylic — why not polyacrylic acid which had been used by Kern and later by Arnold and Overbeek [15]? From the wreckage of planes of World War II vintage, plastic domes made of Perspex (or Lucite) could be salvaged, from which the monomer methylmethacrylate was easily recovered by pyrolytic heating and vacuum distillation of the volatile monomer. This monomer was then used for dental applications or it could be saponified to the pure acid and polymerized to polymethacrylic acid. We described [16] a method for obtaining the free acid from the methyl ester and smoothly re-esterifying with diazomethane. This was important in order to check the basis of early molecular weight determinations of polyelectrolytes. Eliassaf, Silberberg and Katchalsky [17] discovered negative thyxotropy, a phenomenon observed with concentrated polymethacrylic but not with polyacrylic acid solutions. Vigorous stirring with a glass rod of solutions in test tubes led to reversible gelation to a solid-like material. Upon being left to itself the gel relaxed after a while to a clear, freely flowing solution. When Aharon demonstrated this experiment to the 1954 Macromolecular Meeting in Milano (he had the knack of the classical great experimentalists) an Italian professor from Naples excitedly got up in the audience shouting "The miracle of the blood of San Gennaro" which liquefies once yearly in view of the devout.

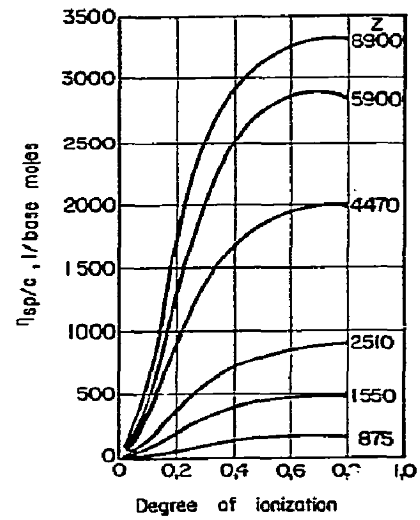

Fig. 1. Dependence of η_{sp}/c of polymethacrylic acid solutions in water on the degree of ionization, for fractions of different degrees of polymerization, Z, at 30°C. Polymer concentration 0.01 base moles/l. From refs. [18,19a].

One day Aharon had the exciting idea that polyelectrolyte molecules could be chemically linked into three-dimensional networks and the huge dimensional changes to which we had ascribed the dramatic increases in viscosity [18,19a] (fig. 1) should be visible on a macroscopic scale (fig. 2) [19b,20]. He immediately had the vision of mechanical work being obtained from chemical energy (from the neutralization reaction of a polymeric acid, for instance) and mechanochemistry was born. A letter was sent off to Werner Kuhn which crossed in the mails with a letter announcing very similar results obtained in Basel. Both results

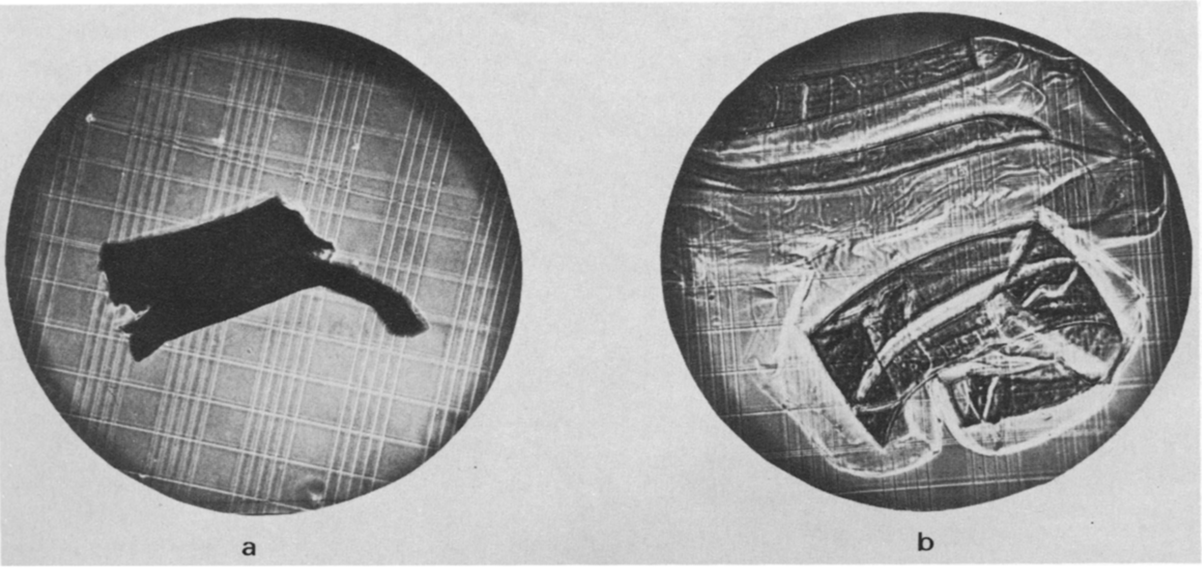

Fig. 2. Polyvinylphosphate fiber; (a) in the contracted state (pH 1–2 upon addition of HCl), fiber contracts in a fraction of a second, (b) in the swollen state (pH 6), fiber expands in 2–3 s. From ref. [19b].

were published in adjoining letters [21,22] and a joint, more detailed report was submitted a little later [23]. Classical polymer theory was extended [24] to an analysis of swelling of polyelectrolyte gels (fig. 3).

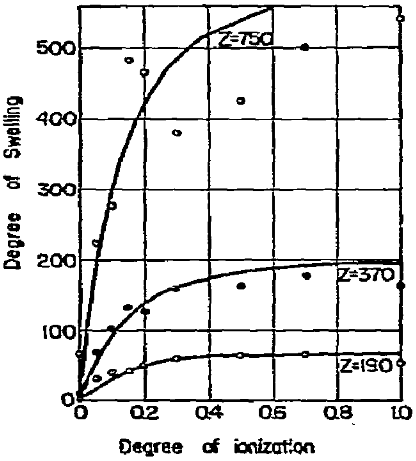

Fig. 3. Equilibrium swelling of gels of polymethacrylic acid crosslinked with divinylbenzene in water, as a function of the degree of ionization, for different degrees of polymerization Z between crosslinks. From ref. [24].

Curiously, about the same time a very similar result was reported by Breitenbach and Karlinger [25]. It seems that credit sometimes is given to the originators of an idea, a discovery. In other instances it appears that they are forgotten and the historical recognition more often applies to those who have carried through the continued development of the original idea.

At about the same time when the activities described here were unfolding Fuoss and his collaborators were active [1,26] in pioneering studies on the viscosity, the conductance, mutual interaction of basic and acidic polyelectrolytes [27] and other fundamental polyelectrolyte studies. Contact between the Katchalsky and the Fuoss groups was established through the literature.

One hot summer day in 1951 when the Fuosses stepped off the gang plank of their boat in Haifa, coming from Egypt, we knew that as far as we in the Polymer Department at the Weizmann Institute in Rehovot were concerned, Israel had entered the scene of international science. Katchalsky later in two lectures reviewed [18] work from the Rehovot group.

I proceeded to spend one year with Ray Fuoss at Yale to work on bolaform electrolytes [28], a term coined by Fuoss to indicate chain-like electrolytes carrying identical charges at both molecular ends. On

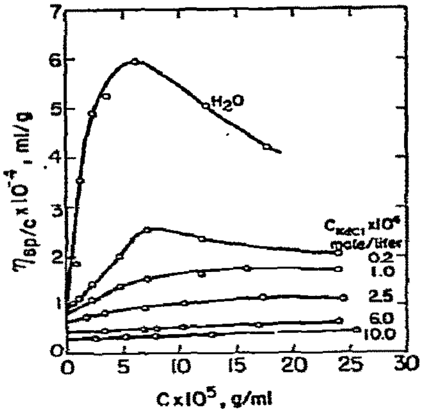

Fig. 4. Reduced specific viscosity η_{sp}/c of aqueous solutions of a partially (61%) quaternized polyvinyl pyridine as a function of polymer and NaCl concentration. To calculate η_{sp}/c (l/base moles) from η_{sp}/c (ml/g) multiply by 0.187. From ref. [29].

my way home, I briefly stopped at Sadron's Centre de Recherches sur les Macromolecules in Strasbourg to investigate a problem concerning the shear and concentration dependence of the viscosity of very dilute solutions of polyelectrolytes. With Jean Pouyet we could show [29] (fig. 4) that the well known steep increase in reduced specific viscosity, η_{sp}/c, with decreasing polyelectrolyte concentrations in aqueous simple salt-free solutions reaches a maximum at very low polyelectrolyte concentrations. I will discuss this phenomenon in more detail below. This topic has in recent years attracted renewed interest, in particular in view of the new tool of neutron scattering [30]. I now conclude my reminiscences of the early phase of polyelectrolyte research a quarter of a century ago. A summary review [31] of this early period is available.

2. Classical non-ionic polymer theory

It will not be possible in the following and within the framework of a relatively short review to give a detailed exposé of the development of all the theories and present the experimental facts which have accumulated in this lively field over the last quarter of a century. This has often been done before and from a variety of points of view. My aim in this and subsequent sections is to present a nutshell discussion of some concepts and experimental approaches which have increased our comprehension of polyelectrolyte behavior. This will be done in non-mathematical terms as far as possible. Later I will briefly consider what the future may bring as a result of renewed interest and powerful new experimental and theoretical tools. To introduce the basic polyelectrolyte coil expansion problem I first briefly digress to an analysis of non-ionic behavior.

Consider a collection of neutral macromolecules in a dilute concentration range ($c \ll c^*$, where c^* is a critical concentration at which macromolecular coils are beginning to overlap). Following Flory [32] I consider the properties of the single macromolecule. In an "ideal" θ solvent long range interactions are compensated, in analogy to the behavior of the Boyle gas in classical thermodynamics, and the chain configurations (characterized by R_g, the root-mean-square radius or "radius of gyration"; R_g can be determined from the angular dependence in light, X-ray and neutron scattering experiments) obey ideal gaussian statistics

$$R_{g0} \propto X^{1/2}; \tag{1}$$

here X is the number of "units" of which the chain is composed; we use zero subscript for R_g to indicate that these are unperturbed dimensions in the θ solvent, and the *linear coil expansion factor* $\alpha \equiv R_g/R_{g0}$ equals unity. Under these conditions the volume excluded by the macromolecule (both intra- and intermolecularly) vanishes. Therefore, should we now increase the concentration c to the critical overlap concentration c^* and beyond, the macromolecules will interpenetrate as they do not interfere greatly with each other. In analogy to the ideal gas law the reduced osmotic pressure Π/c equals RT/M.

The value of R_{g0} in dilute solutions is determined by local short range interactions (steric hindrances to rotation around bonds, for instance) and a convenient quantity to define chain properties is the statistical element of Kuhn [33a] or the Kratky-Porod [34] persistence length. Many years ago Kuhn [33b] and Flory [32] had predicted that in the extreme case of the pure amorphous polymer systems, ideal conformations should also prevail; this has recently unambiguously been confirmed by neutron scattering experiments in which the scattering from a small number of non-deuterated polystyrene [35] and polymethylmethacrylate [36] molecules could be analyzed, when these were dispersed (in simulation of a "dilute" solution experiment) in a large excess of deuterated macromolecules.

If we depart from ideal θ conditions and introduce repulsive interactions between chain elements (by the use of a "good" solvent, for instance, in which polymer–solvent contacts in solution are preferred over polymer–polymer contacts) then R_g increases beyond the ideal, unperturbed value, and α assumes values larger than unity. The intramolecular excluded volume theory of Flory leads to the now classical expression

$$\alpha^5 - \alpha^3 = Cz \tag{2}$$

for the expansion parameter α in neutral polymers, where C is a constant which depends to some extent on the assumed distribution of segments around the molecular center of mass, in the spherically symmetric cloud model of segments assumed by Flory; z is a dimensionless variable

$$z = (3/2\pi)^{3/2}\beta X^2/R_{g0}^3, \tag{3}$$

where β is the mutually excluded volume for a pair of segments (the single contact term $\beta X^2/2$ is the total volume excluded pairwise by one macromolecule and is furthermore invariant to a change in segment size). Combination of eqs. (1) to (3) shows that in the asymptotic limit of large X, R_g increases with $X^{3/5}$ for chains with excluded volume.

The unperturbed intrinsic viscosity $[\eta]_\theta$ is equal to

$$[\eta]_\theta = \Phi R_{g0}^3/M, \tag{4}$$

where Φ is a dimensionless constant first introduced by Kirkwood and Riseman, and M is the molecular weight. The proportionality of M to X and of R_{g0} to $X^{1/2}$ leads to the dependence of $[\eta]_\theta$ on $X^{1/2}$ or $M^{1/2}$. For chains with excluded volume

$$[\eta]/[\eta]_\theta \equiv \alpha_\eta^3, \tag{5}$$

and we now easily derive that $[\eta]$ increases with $M^{0.8}$ for neutral chains in good solvents if α and α_η can be taken to be identical.

I have above considered the excluded volume properties of single non-ionic chains. What happens when intermolecular interactions become noticeable? Very dilute solutions (c is still appreciably smaller than c^*) are well behaved and the osmotic pressure Π, for instance can be expanded in a virial series

$$\Pi/RTc = 1/M + A_2c + \ldots \tag{6}$$

where A_2 is the second virial coefficient which vanishes when the excluded volume is equal to zero. (It was Flory's basic contention that both the intra- and intermolecular excluded volumes vanish at the identical θ conditions.) As was shown by Debye many years ago, the derivative of Π with respect to c determines the intensity of scattered radiation at zero scattering angle – scattering experiments in addition to providing information about molecular size and size distribution, thus represent a valuable way of obtaining thermodynamic information about interactions between solute particles.

In terms of the parameters used for the intramolecular interactions

$$A_2 = (N_{Av}/M^2)(\beta X^2/2)F(z), \tag{7}$$

where N_{Av} is Avogadro's number and $F(z)$ is a dimensionless function of z, for higher order molecular contacts; $F(z)$ reduces to unity when $z \to 0$.

More concentrated, semi-dilute, solutions, where c is of the order of c^* and the domains of macromolecular chains overlap, present great interest both experimentally and theoretically. In a recent paper [37] which attempts to go beyond the original Flory and Huggins classical mean-field considerations, neutron scattering experiments are presented and interpreted in terms of a scaling procedure introduced by des Cloiseaux.

3. Polyelectrolyte experiments

We are now ready to consider the special properties of polyelectrolyte systems. Consider a single macromolcular chain to which equally or irregularly spaced charges have been attached along the chain (by a chemical procedure such as sulfonation of polystyrene for instance, or by ionization of a carboxylic acid or base). From the early days of polyelectrolyte research, it was known that the viscosity of such solutions increases many fold. This could be related to coil expansion caused by fixed-charge repulsion following ionization (fig. 5) or, in particular in the absence of added salts (in low-conductivity solutions), to an electroviscous effect previously associated with colloid particle particle interactions. Whereas in non-ionic polymers the reduced specific viscosity η_{sp}/c decreases with

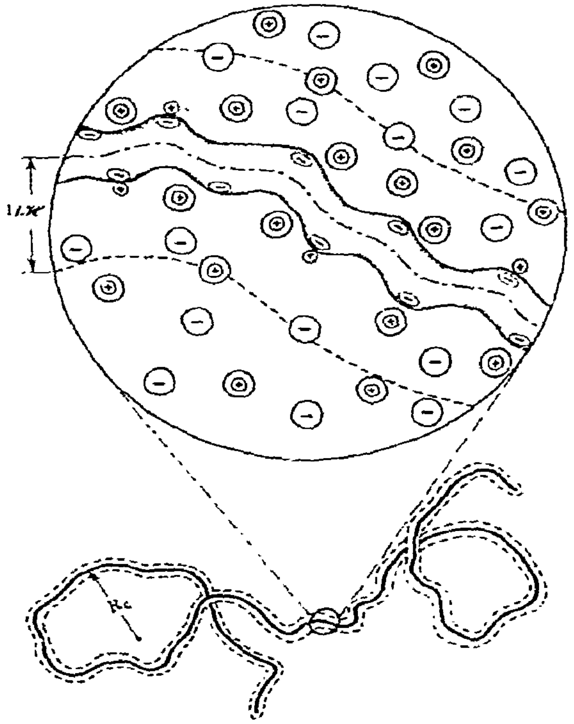

Fig. 5. Schematic drawing of polyelectrolyte in the presence of 1 : 1 simple electrolytes. Symbols: ⊝ , fixed charge on polyanion; ⊕ , dehydrated counterion site bound to polyanion; ◎, hydrated counterion; ⊖ , coion. Dashed line is drawn at Debye–Hückel reciprocal shielding length, $1/\kappa$; R_C denotes the local radius of curvature of the chain. From ref. [66].

decreasing concentration, c, in salt-free polyelectrolytes η_{sp}/c increases strongly with decreasing concentration apparently (it was first believed) without limit. Only at extremely low polyelectrolyte concentration is a maximum reached and η_{sp}/c thereafter decreases with further decreasing concentration (fig. 4). The viscosity is often shear-dependent and extrapolation to vanishing rate of shear is mandatory.

If we want to understand the dependence of η_{sp}/c on concentration depicted in fig. 4, then a few quantitative (or rather semiquantitative) remarks are in order. Consider the solutions in pure water first. We are investigating a medium molecular weight polymer of vinylpyridine (fig. 6), consisting of 7700 monomer units, 61% of which are quaternized with n-butyl bromide. The molecular weight is 1.45×10^6, the

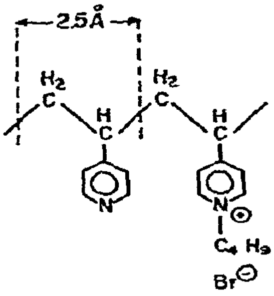

Fig. 6.

length L of the all *trans* extended conformation is 1.97×10^{-4} cm, and the average charge density is therefore roughly one electronic charge per 4.2 Å (there is a fine distinction here between a partially quaternized pyridinic polymer, in which discrete fixed charges in a particular distribution can, in principle, be observed on a single macromolecule, and a partially ionized polycarboxylic acid for instance, in which the distribution along the chain of the ionized and non-ionized groups may assume a large number of statistical configurations [14] as a result of the fast and reversible ionization process).

If we indeed assume that electrostatic repulsion results in maximum stretching of the particles, then by a well known equation for the viscosity of very long thin rods,

$$[\eta] = 4\pi N_a L^3 / 90\, M \ln 2p \tag{8}$$

(p is the axial ratio L/d, where d is the thickness of the molecule), we find $[\eta]$ equal to 4.6 and 5.4×10^4 ml/g for values of d of 2.5 and 10 Å, respectively (the calculation is rather insensitive to the value assumed for d). How low must the concentration be to avoid overlap of macromolecular domains, even if we disregard the charged nature of the particles? A simple calculation shows that, for the case of fully extended chains and the particular macromolecules considered, the value of c^* for molecular domains just touching is 3×10^{-7} g/ml ($\eta_{rel} = \eta_{sp} + 1$ would be 1.015, with $[\eta] \approx 5 \times 10^4$ ml/g, under these conditions)!

These are enormous values of η_{sp}/c and extremely low concentrations. In practice (fig. 4) we find in water a maximum of $\eta_{sp}/c = 6 \times 10^4$ ml/g (higher than expected for stretched rods), at 6×10^{-5} g/ml

(η_{rel} equals 4.6 at this rather low concentration); the concentration of charged groups is about 2×10^{-4} moles/ℓ. With further decrease in concentration η_{sp}/c drops to about 10^4 ml/g. Similar, and also slightly lower values are obtained by addition of minute (of the order of 10^{-4} M) amounts of NaCl. At this low salt concentration the maximum in η_{sp}/c has completely disappeared. The charged molecules appear to be expanded to about half their extended length (corresponding to a value of η_{sp}/c of about 10^4 ml/g). The additional viscosity increase in the pure aqueous medium apparently derives from long range electroviscous counterion atmosphere interaction and may be depressed by either increasing the concentration of macromolecules or addition of salt. As the polyelectrolyte molecules are not fully extended in solution c^* is shifted to somewhat higher values (about one order of magnitude) in the present case. The linear expansion factor α_η over θ dimensions [eq. (5)] is estimated, by comparison with the viscosity in θ solvents, to be about 6, whereas in non-ionic polymers, values of 2 are rarely exceeded. The viscosities (fig. 1) of polymethacrylic acid as a function of molecular weight [18,19a] were measured at 10^{-2} base mole/ℓ, that is at a considerably higher concentration than the viscosities in fig. 4. These solutions therefore properly fall in the range of the semi-dilute solutions and the molecular weight dependence should be related to a theory for overlapping chains (shear corrections for the viscosity had not been considered in this early work).

In distinction to the short ranged potentials in non-ionic macromolecular solutions, electrostatic repulsions in dilute salt-free polyelectrolyte systems are long ranged and the viscosity of the dilute salt-free polyelectrolyte solution thus, to a large degree, measures interionic interactions between polyions enclosed by counterion clouds rather than the energy expended by the friction of the single macromolecular ion coils. The sharp decrease in η_{sp}/c at very low polyelectrolyte concentrations (fig. 4) is most likely caused by the fact that at these low concentrations self-ionization of the solvent and other ionic impurities (dissolved carbon dioxide, for instance) provide significant electrostatic screening and effectively buffer the interionic interactions; (plots of η_{sp}/c increasing linearly with concentration over the whole range of c can be obtained [38] by a device called isoionic dilution in which a constant ionic strength of mobile ions — excluding the fixed charges — is maintained, with the additional empirical assumption that some of the counterions are "bound" to the polyelectrolyte chains). In the ascending limb with decreasing polyelectrolyte concentration, and in keeping with simple electrolyte theory, $\eta_{sp}/c^{1/2}$ is a more appropriate parameter to plot then η_{sp}/c.

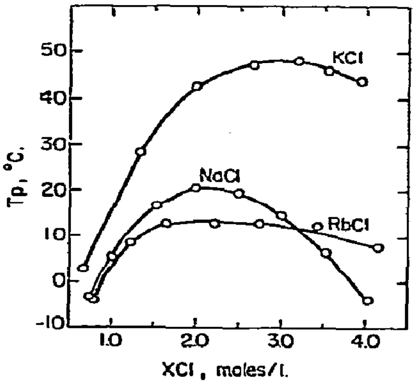

Fig. 7. Liquid–liquid phase separation temperatures T_p at constant concentration (0.274 base mole/ℓ) of polyvinylsulfonic acid, with various electrolytes XCl (X = Na, Rb, K). From ref. [39].

Addition of a little salt provides screening, reduces the range of electrostatic forces and restores normal behavior; η_{sp}/c now increases with c over the whole range of c. The osmotic pressure Π may be expanded in a virial series [eq. (6)] which was not possible in the salt-free case for which a totally different expression applies [42]. Scattering experiments become meaningful again. Addition of a large amount of salt reduces the behavior of charged macromolecules to that of non-ionic chains. Even in highly ionized polyvinylsulfonate [39] ion-specific liquid–liquid phase separation may be induced (fig. 7); ideal θ conditions have been achieved for this [40] and other systems [66] which fulfil all the requirements postulated by Flory for the neutral chains.

The ratio of unperturbed dimensions at the θ temperature to the value for free rotation around bonds is very similar to that found in non-ionic polymers. Screening of the elecrostatic charges reduces the long range coulombic potentials to short range screened potentials; the interesting problems remaining now concern the very specific interactions between large and small ions in solution. The polyion, simple salt, water systems are multicomponent and interesting problems arise, the thermodynamic aspects of which have been treated by Casassa and the present author [41]. The simples case is that of a three-component solution [42] and no further conceptual difficulties arise by extension to any number of components.

The high intra- and intermolecular interaction in salt-free polyelectrolyte solutions is equivalent to a huge effective excluded volume. Long range interactions in non-ionic polymers and long range electrostatic interactions in polyelectrolytes are then in some ways conceptually equivalent. The advantage of studying the ionic polymers is that the variation of simple salt concentration constitutes a good handle to study the effect of molecular interactions. Once θ conditions are achieved, short range interactions determine the basic "stiffness" of the macromolecules and the value of the Kratky–Prood persistence length under these conditions may to a considerable extent be determined by steric structure factors.

What happens when we attempt to concentrate salt-free polyelectrolyte solutions into the semi-dilute range is another story. We have already seen that non-ionic polymers in good solvents in dilute solutions will put-up a fierce resistence to interpenetration of chains. Yet, luckily for the undaunted investigators [43] polyelectrolytes are more obliging than non-ionic polymers. Whereas the excluded volume leads to quasi-impenetrable sphere behavior in the case of neutral macromolecules [32] the repulsive long range electrostatic potential is screened as a result of the increasing number of ions in solution, with increasing polyelectrolyte concentration, even in the absence of added simple salt. The problem remains complex, yet assumes interesting possibilities in terms of the neutron scattering experiments which can now conveniently be performed. In a semi-dilute solution, a small fraction of (to all intents and purposes identical) polyelectrolyte molecules can be labelled by deuterium substitution and their conformational properties observed in as far as these are affected by the presence of a large excess of identical nonlabelled macromolecules (both this and the inverse labelling experiments can be performed).

For the very dilute range de Gennes et al. [43] predict an ordered three-dimensional lattice and Cotton and Moan observe [44] (by studying the angular dependence of neutron scattering) an intensity peak which may correspond to long range ordering in very dilute ionized polymethacrylic acid solutions, dissolved in heavy water. In another study [45] long range ordering due to repulsive coulombic interactions was observed by conventional light scattering and photon correlation spectroscopy in aqueous dispersions of charged polystyrene spheres, at very low ionic strength; the scattered intensity exhibited maxima similar to those found in the structure factors of simple liquids determined by X-ray or neutron scattering.

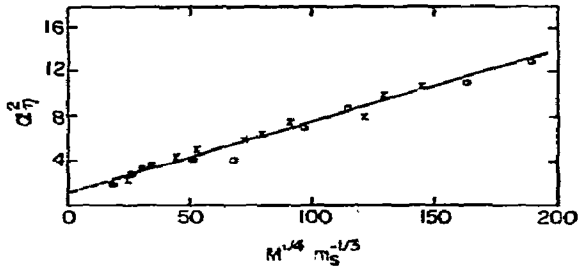

Fig. 8. Dependence of expansion factor α_η^2 on $M^{1/4} m_s^{-1/3}$ for samples of potassium polystyrenesulfonate; filled circles, 0.5 M KCl; empty circles 0.01 KCl; crosses, all other salt concentrations. From ref. [57].

4. Polyelectrolyte theories

The history of theoretical treatments of polyelectrolyte behavior goes back to the papers of Kuhn, Künzle and Katchalsky [13], who calculated the electrostatic energy of a salt-free polyelectrolyte model, in an extension of the Kuhn statistical chain theory (later this was extended [46,47] to cover the situation in the presence of salt) and of Hermans and Overbeek [48] who represented the polyelectrolyte molecule by a porous, flexible coil. Similar models, which are based on a Donnan equilibrium concept (we imagine the polymer coil to be surrounded by an imaginary membrane permeable to small ions only) were propounded by Kimball, Cutler and Samelson [49], and by Flory and Osterheld [50]. Wall and Berkovitz [51] gave a numerical solution (one of the earliest applications of the computer to polymer problems) of the Poisson–Boltzmann equation for the porous sphere and Lifson [52] presented a simple perturbation calculation which gave precisely the same results. The trouble was that neither flexible coil nor porous sphere model proved adequate to explain the configurational properties of polyelectrolyte molecules. Although some other quantities, such as titration behavior and distribution of small ions could fairly accurately be accounted for by introducing an "effective" charge or some other adjustable parameter, the earlier theoretical work predicted that charged macromolecules would already be completely extended at very low degrees of charge, in complete disagreement with well executed and well interpreted experiments. Polyelectrolyte coils are expanded beyond ideal random coil conformations, but (as we have seen above) by no means are they ever stretched to their full length. That stretching occurs is clear from the study of the swelling of crosslinked polyelectrolyte gels (figs. 2 and 3). Here though one should realize that swelling is to a large extent caused by the osmotic Donnan effect of the small ions trapped in the gel because of the requirement of electroneutrality, rather than as a result of honest-to-goodness "muscle" flexing (intrinsic stiffening) of the macromolecular chains.

A new theoretical approach introduced the rigid rod or cell model of polyelectrolyte solutions [53, 54]. It was based on the realization that whereas polyelectrolyte macromolecules flexibly bend over large distances, they are fairly rigid over short distances along the chain. Commendable results were achieved with respect to properties dependent on the electrostatic potential, although once more, configurational properties were not easily comprehended. Much later, Alexandrowicz [55,56] presented a theory for polyelectrolyte configuration which could be tested with some degree of successs.

Alexandrowicz predicts α^2 to depend linearly on $z^{1/2}$ while z should be proportional to $M^{1/2}/m_s^{2/3}$ (m_s is the concentration of added salt). We find (fig. 8) [57] for potassium polystyrene sulfonate in KCl

$$\alpha_\eta^2 = 6.4 \times 10^{-2} M^{1/4} m_s^{-1/3} + 1.1, \tag{9}$$

in agreement with the prediction of Alexandrowicz, for $\alpha^2 \geqslant 2$. In the above formulation the effects of long and short range interactions are separated. A similar test of the viscosity data of Takahashi, Kato and Nagasawa [58] for sodium polystyrene sulfonate in NaCl yields a comparable relationship. The agreement is pleasing yet it cannot be taken as a proof for this theory to constitute a simple and unique solution to a complicated problem.

The Poisson–Boltzmann equation could be numerically solved [59,60] and in particular applied to DNA, a stiff backbone polyelectrolyte macromolecules with well defined geometry. Some success was enjoyed by postulating additivity concepts of various kinds which stated that, within reasonable limitations, some colligative properties of polyelectrolyte solutions can be additively constructed from the properties of salt-free polyelectrolyte and simple-salt electrolyte solutions [61]. Another useful concept was the idea introduced and reviewed by Oosawa [62], and by Manning [63] that, when the charge density on the macromolecular chains increases beyond a certain critical value, condensation of counterions on the macromolecules takes place, and the charge is effectively reduced. Ions which do not condense in the above way remain free in solution and behave in classical Debye–Hückel simple electrolyte fashion. I purposely chose not to go into the details of the theories presented as this has been done many times before and comparative evaluations of polyelectrolyte behavior have repeatedly been given in the references quoted. We cannot escape the conclusion that, in spite of the tremendous effort devoted to the problem in the least quarter of the century, polyelectrolyte theory still is in a developing state – the forty years of wandering in the desert are not yet over. No simple parameter-free equivalent of the limiting slope in the Debye–Hückel theory of simple electrolyte exists.

5. A guide to the perplexed

Reviews on topics of interest appear at regular intervals and invariably conform to similar patterns. Here I have tried to strike a different note, first by presenting some historical details from personal recollections and then by reviewing some limited, yet crucial, polyelectrolyte problems, the solution of which has fascinated workers for many years. Lest I be accused of undue personal bias, and in order to provide a guide to the perplexed (with apologies to Maimonides) to the complexity of polyelectrolyte behavior, I will conclude by listing a number of pertinent works reviewing diverse aspects of polyelectrolyte work.

The early contributions on molecular expansion, calculation of the electrostatic free energy, crosslinked networks, colligative and transport properties were summarized in the reviews of Katchalsky [18], of Fuoss [1] and of Eisenberg and Fuoss [28]. Rice and Nagasawa (with a contribution by Morawetz) [74] in 1961 produced a full-size monograph on polyelectrolyte solutions embodying review and critique of the Harris–Rice and earlier theoretical approaches. Katchalsky, Alexandrowicz and Kedem [61] in 1966 and Katchalsky [65] in 1971 summarized the colligative and transport properties of polyelectrolyte solutions. An important article by Armstrong and Strauss [66] in 1959 critically reviews theories of equilibrium and transport properties and presents a short section on applications.

This is a good place to look for analysis of membrane distribution parameters and ion binding (both of the ion atmosphere and the site binding type). The concept of "ion condensation" is made more precise in the book by Oosawa [62] and the review of Manning [63] in 1972, who also critically reviews developments in the controversial topic, first introduced by Wall [67–69] and his collaborators in 1950, on the alleged entrapment (or undue residence time) of small ions in polyelectrolyte coils. The review of Crescenzi [70] in 1968 is valuable for its discussion, inter alia, of rates of reaction between polyelectrolyte and simple substrates as influenced by the polyelectrolyte potential. Similar and other considerations were presented by Morawetz [71] in 1975.

A number of articles of topical interest appear in the proceedings of a conference, edited by Selegny [72]. Biological macromolecules and polyelectrolytes in solution, in particular from the point of view of the theory of multicomponent solutions, are discussed in a recent monograph of the present author [42]. A book on the physical properties and structure of ion containing polymers in bulk and in solution by A. Eisenberg and King [73] is in press. And we can always rely on the text of Tanford [74] for a wealth of references and information. A review by Overbeek, on polyelectrolytes, past, present and future, has just appeared [75].

I was stimulated to put down these considerations after listening to P. de Gennes on a new look at nonionic polymers and some more speculative considerations [43] about the properties of polyelectrolyte solutions over a wide range of concentrations. Whether these theories will, or will not, lead to new results, will or will not solve old controversies, will or will not present the long awaited elegant solution to the polyelectrolyte problem, remains to be seen. I am happy to note that polyelectrolyte studies are still under active investigation and many topics of great interest have not even been mentioned in the present review. Applications and ramifications extend, on the one hand, into biological and, on the other, into industrial aspects of scientific research. It is not a gross oversimplification to state that, with all due respect to carbohydrates, lipids and other hydrophobic structures, we live in an aqueous world in which charge-carrying polymers and charge–charge interactions, whether in the bulk or at membrane interfaces, play a major role.

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