

# POLYELECTROLYTES, PAST, PRESENT AND FUTURE

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**Abstract**—In the introduction the close relation between polyelectrolytes and hydrophilic colloids is stressed. A survey is given of present day polyelectrolyte knowledge as accumulated since about 1940. In this respect mention is made of osmotic pressure, Donnan pressure, light scattering, titration, activity of small ions in polyelectrolyte solutions, swelling and viscosity, protective action and sensitization, electrophoresis and electrical conductance, and dielectric polarization. A preference is indicated for a cylinder model with the possibility of counterion condensation above a porous sphere model and a list of gaps in our knowledge with a few suggestions for further applications are given.

## INTRODUCTION

Some natural polyelectrolytes, such as glue and gums, have been used from time immemorial as thickeners and the use of gum as a protective colloid is as old as the use of India ink, which is finely ground soot, suspended in water and stabilized with gum arabic. The term colloid was coined by Graham<sup>1</sup> who derived it from the Greek word for glue (κόλλα).

In early colloid research most systems investigated had water as the dispersion medium and it was soon recognized that a rather sharp division into two main groups, the hydrophobic and the hydrophilic colloids, was indicated. Later, with the introduction of solvents other than water, the two groups were extended to lyophobic and lyophilic colloids.

The hydrophilic (lyophilic) colloids are truly soluble in water (the solvent) and derive their colloidal nature from the huge size of their molecules or from reversible association of many small molecules to micelles. In either case the solubility in water requires the presence of polar groups in the molecules, and since these polar groups are often ionizable, especially in natural hydrophilic colloids, it is self evident that a great part of the early research on lyophilic systems dealt with polyelectrolytes in aqueous solution.

It had been shown that the presence of an electric charge on the particles of hydrophobic colloids was essential for their existence (Freundlich<sup>2</sup> called them *electrocratic*). So it was only natural for Kruyt and Bungenberg de Jong,<sup>3</sup> when they started their research on agar-agar in 1919, to look for effects of the electric charge of the particles. In that time electrophoresis was a difficult and very time consuming technique, but they found that the viscosity of agar-agar solutions decreased in a pronounced way on the addition of electrolytes and that the valence of the cation was the determining factor in this decrease (see Fig. 1). They recognized the rule of Schulze and Hardy,<sup>4</sup> (effect much more than proportional to the valence of the cation) well known from the research on the stability of hydrophobic colloids and explained their findings on the basis of an eqn (1) derived in 1916 by Von Smoluchowski<sup>5</sup> as an extension of Einstein's eqn<sup>6</sup> for the viscosity of a suspension of spherical particles.

$$\frac{\eta_s - \eta_0}{\eta_0} = 2.5\varphi \left[ 1 + \frac{1}{\eta_0 \kappa r^2} \left( \frac{\epsilon \zeta}{2\pi} \right)^2 \right]. \quad (1)$$

In this equation  $\eta_s$  and  $\eta_0$  are the viscosity of the suspension and the solvent resp.  $\varphi$  is the volume fraction

of the spheres,  $r$  their radius,  $\kappa$  the specific conductance of the solution,  $\epsilon$  its dielectric constant and  $\zeta$  the surface potential (zeta-potential) of the particles. In Von Smoluchowski's theory the increase of the viscosity above the Einstein value is due to the distortion of the spherical electrical double layer into a quadrupole in the field of flow.

After the discovery that small particles, such as quartz, carbon, or oil droplets adsorb hydrophilic colloids and assume an electrophoretic mobility similar to that of the free hydrophilic colloid, microscopic electrophoresis became a favourite tool for studying charge and zeta-potential of these substances. Figure 2 shows<sup>7</sup> how lead nitrate affects the electrophoretic mobility of a variety of carriers, but that after addition of only 0.09% of N-arabinate all curves come together and obviously this curve represents the mobility of adsorbed arabinic acid. Figure 3 shows<sup>7</sup> how the concentration of charge reversal (zero electrophoretic mobility) by hexamine-cobalt chloride changes from its low value for quartz to a much higher one characteristic for arabinic acid on increasing the

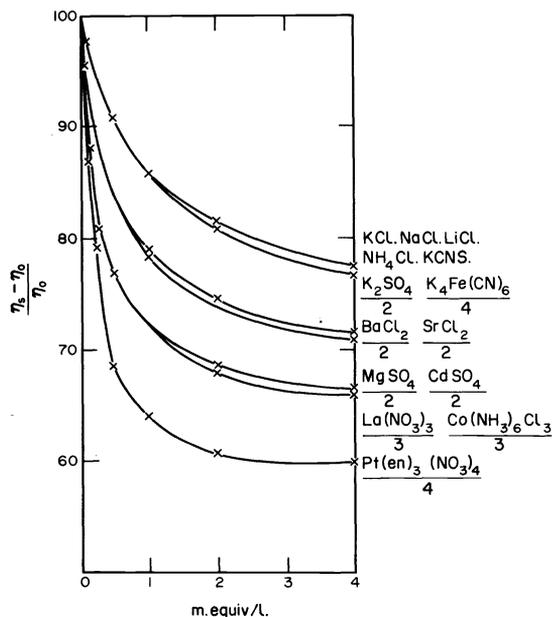


Fig. 1. Relative increase of the viscosity of a 0.14% solution of agar-agar at 50°C over the viscosity of the solvent as a function of the concentration (in m-equiv/l of added electrolyte). Pt(en)<sub>3</sub> stands for the four valent platinum (ethylenediamine)<sub>3</sub> ion.

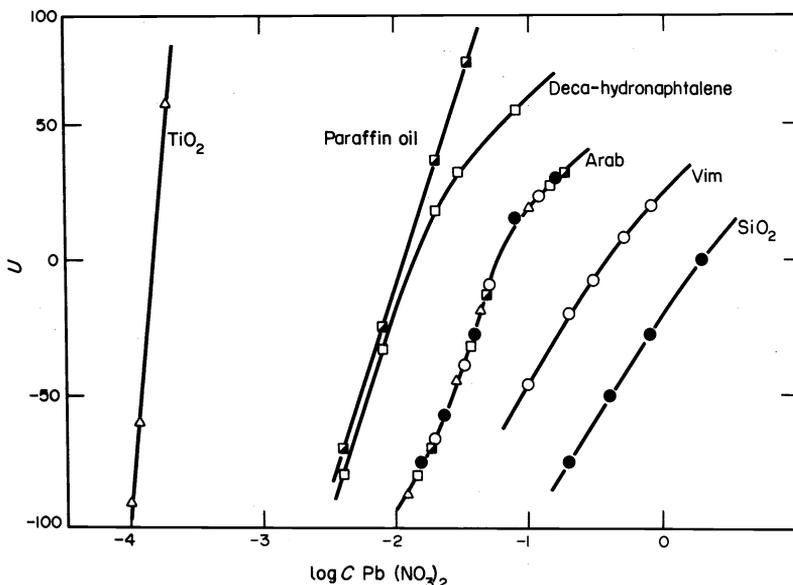


Fig. 2. Electrophoretic mobility,  $U$ , in arbitrary units, of a number of different carrier particles and of these particles in a 0.09% Na arabinat solution as affected by the concentration of lead nitrate in equiv/l.

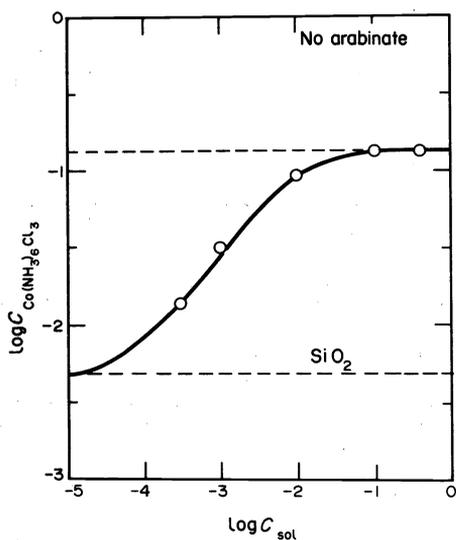


Fig. 3. Logarithm of the concentration of hexamine-cobalt chloride in equiv/l needed for charge reversal (zero electrophoretic mobility) of quartz particles in solutions of Na-arabinate.  $C_{sot}$  expressed in %.

arabinate concentration from  $10^{-5}$  to 0.1%. Kruyt and especially Bungenberg de Jong and his school<sup>8</sup> continued their work with hydrophilic colloids using agar-agar, gums, gelatine and other long-chain polyelectrolytes, although in the first years of this research they still considered these colloids as aggregates rather than as macromolecules.

The physical chemical approach to proteins, in particular to soluble corpuscular proteins profited from the development of refined new instrumentation. I mention here Svedberg's ultracentrifuge<sup>9</sup> (1926), Tiselius' electrophoresis<sup>10</sup> method (1930) and light scattering, as first applied by Putzeys and Brosteaux<sup>11</sup> (1935) to proteins. These new techniques, the better methods of separation and purification and, above all, the fact that many proteins

are pure chemical entities with a well defined molecular weight allowed proteins to become for a time the main objects of polyelectrolyte research, although the research was aimed more at structure and function of proteins than at their properties as electrolytes.

In the Dutch school the further study of viscosity, electrophoretic mobility, turbidity and precipitation of polyelectrolytes as affected by low molecular weight salt led to the appreciation of the charge density (as characterized by the equivalent weight) and the nature of the charged groups ("phosphate-, carboxyl-, and sulphate colloids") as determining factors. It was found that reversal of charge caused by "adsorption" of cations often was accompanied by precipitation and the higher the charge density the lower the valence of the cation that would suffice for precipitation<sup>12</sup> (see Fig. 4). In addition to the influence of the valence, specific influences of the nature of the cations on the concentration needed to obtain charge reversal were found.<sup>13</sup> For example, for carboxyl- and sulphate colloids the concentration of charge reversal increases in the order Ba, Sr, Ca, Mg, K, Na, Li but for phosphate-colloids the order in the alkaline earth ions is irregular and for the alkali ions it is Li, Na, K.

These polyelectrolytes are not only precipitated by multivalent small ions, but also by polyions of opposite sign. The precipitates are liquid, although sometimes quite viscous. They are called coacervates, or complex coacervates in the case of mutual precipitation of oppositely charged polyions. Here again the charge density proved to be a very important factor as exemplified by Fig. 5, in which the complex-coacervation between gum arabic (negative) and gelatin (positive below pH = 5) is shown as a decrease in viscosity below the additive value.<sup>14</sup> Going from pH = 5 where gelatin has no charge, but gum arabic is strongly negative, via pH = 3.5 (gelatin strongly positive, gum arabic still rather strongly negative) to pH = 1.2 where gelatin is positive, but gum arabic practically uncharged, the complexcoacervation starts at zero, goes through a maximum and returns to zero. Addition of low molecular weight salts, which screen the charges of the polyions suppresses complex-coacervation.

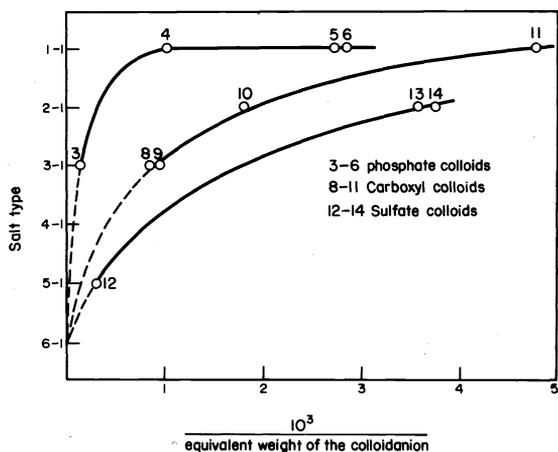


Fig. 4. Relation between tendency to precipitation and equivalent weight of the polyanion (colloidanion). The points on the graph correspond to the salt of the highest valence type that will not precipitate the polyion. 3 = soya bean phosphatide I (alcohol soluble); 4 = soya bean phosphatide II (alcohol insoluble); 5 = NaDNA (thymus); 6 = NaRNA (yeast); 8 = Na arabinatate; 9 = Na pectinate; 10 = Na semenlini mucilage; 11 = Na pectate; 12 = Na agar; 13 = K chondroitin sulphate; 14 = Na carragene; 3 and 4 are association colloids, not polyelectrolytes, but they fit in the whole picture.

With two polyelectrolytes of high charge density very dense coacervates are formed, which can be cast in stable membranes.<sup>15</sup> Another application of the coacervates is based on the very low interfacial tension (0.001–0.01 dyn cm<sup>-1</sup>). It allows the coacervate to envelop substances of low polarity and is the basis of the so-called micro-encapsulation.<sup>16</sup>

DEVELOPMENTS SINCE 1945

During the development of polymer science in the thirties and early forties (Staudinger,<sup>17</sup> Carothers,<sup>18</sup> Kuhn<sup>19</sup>) little attention was given to the behavior of linear polyelectrolytes, with the notable exception of a few papers by Kern<sup>20</sup> on the osmotic pressure, activity of counterions, electrical conductance and viscosity of synthetic polyacids.

But at a symposium, held in Liège (Belgium) in 1948 at the occasion of H. Mark's presence there as a visiting professor, it became clear that polyelectrolytes had caught the attention of several groups of scientists, who worked at achieving a synthesis between the theory of electrolytes and the electrical double layer and the statistical and thermodynamic treatment of coiled polymer chains.

In papers by Kuhn, Künzle and Katchalsky<sup>21</sup> and by Hermans and the present author<sup>22</sup> a treatment was given of the swelling and shrinking of polyelectrolyte coils under the influence of their charge (or degree of dissociation) and the presence of salts, leading to an explanation of the electroviscous effect, and of the influence of charge and salts on the titration curve. At the presentation of these papers H. Mark remarked that R. Fuoss was working on the same subjects at Yale University.

From that time on polyelectrolyte research developed rapidly, a good part of it by the able hands of Katchalsky and his well chosen coworkers.

The central concepts in understanding polyelectrolyte

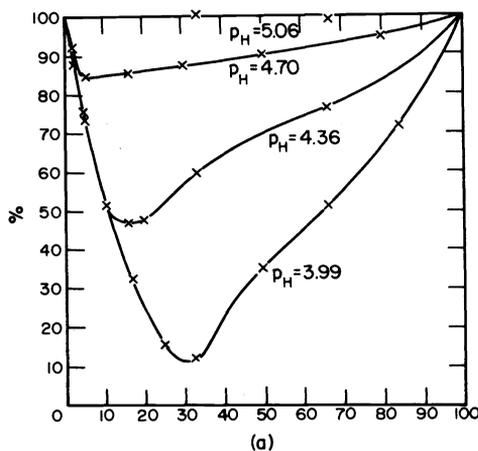
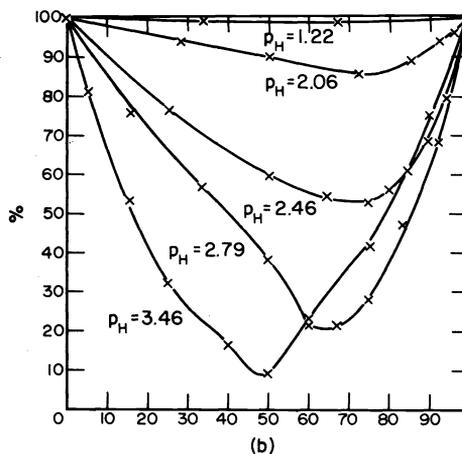


Fig. 5. Effect of pH on the viscosity of mixtures of 0.67% solutions of gelatin (G) and gum arabic (A) as an indication of complex-coacervation. Ordinates: measured value of  $(\eta_s - \eta_0)/\eta_0$  as a percentage of the calculated value of  $(\eta_s - \eta_0)/\eta_0$  assuming additivity. Abscissae: mixing proportion of G and A, expressed in % A. The lower the value of the ordinate, the stronger the tendency to coacervation, i.e. the higher the polyion concentration in the coacervate.

behavior are:

(a) as a consequence of the concentration of electric charges along the polyelectrolyte chain, there is strong electrical interaction amongst these charges and the surrounding small ions,

(b) therefore, the solutions show large non-idealities in their osmotic pressure, ion activities and electrical transport,

(c) moreover, the coils will swell under the influence of the repulsion amongst the charges on the chain, as modified, of course, by the surrounding ionic atmospheres,

(d) this swelling will increase the viscosity of the solutions and express itself in the swelling of polyelectrolyte gels.

In the quantitative theory the following problems must be solved.

(e) How does one describe the electrical free energy of a coil in a given conformation with its ionic atmosphere?

(f) Which model for the coil is applicable?

(g) Is it sufficient to assume complete dissociation between polyion and counterions, with only electrostatic binding or should some site binding be introduced?

(h) Even if no site binding has to be introduced, should the finite size of the small ions be introduced or is a description as point charges adequate?

Before trying to answer these questions, we shall first present briefly some of the experimental observations.

#### Osmotic pressure

The ideal osmotic pressure,  $\pi_{id}$ , of a very dilute, saltfree solution of  $c_p$  mol/unit volume of a polyelectrolyte of degree of polymerization,  $P$ , with  $P$  ionizable groups per molecule (the extension to different numbers for the degree of polymerization and number of ionizable groups is trivial) of which the fraction  $\alpha$  is actually ionized would be

$$\pi_{id} = c_p RT(1 + \alpha P). \quad (2)$$

The actual osmotic pressure,  $\pi$ , is considerably lower and this can be described by assigning an osmotic coefficient,  $\gamma_p$ , to the counterions, leading to

$$\pi = c_p RT(1 + \gamma_p \alpha P) \approx c_p RT \cdot \gamma_p \alpha P \quad (3)$$

where the second form is a very good approximation since  $P \gg 1$ . Introducing the concentration  $c_m = c_p P$  in monomoles per unit volume, we have:

$$\pi = c_m RT \gamma_p \alpha. \quad (4)$$

It is found that  $\gamma_p$  is nearly independent of the degree of polymerization, it decreases with increasing charge density (increasing  $\alpha$ ) and except for the lowest values of  $\alpha$ ,  $\gamma_p \alpha$  is nearly constant. See Katchalsky, Alexandrowicz and Kedem.<sup>23</sup>

The quantity,  $\gamma_p c_m \alpha$ , may be interpreted as the counterion concentration midway between two polyions, i.e. at a location where the electric field strength is zero.

When salt (for simplicity we consider only monovalent salts), is added to the polyelectrolyte solution it is found that the osmotic pressures are additive. So

$$\pi_{tot} = \pi_p + \pi_s \quad (5)$$

where  $\pi_{tot}$  is the observed osmotic pressure in a mixture where polyelectrolyte and salt, if present alone, would exert osmotic pressures of  $\pi_p$  and  $\pi_s$ , respectively.

#### Donnan pressure

When the osmotic pressure is determined with a membrane, permeable to the solvent and all small ions, but impermeable to the polyions, we obtain the Donnan pressure or oncotic pressure. The solution outside the membrane then contains a salt concentration  $c'_s$  in equilibrium with  $c_p$  and  $c_s$  inside the membrane. It is useful to describe this equilibrium as an expulsion of some salt from the neighbourhood of the polyions, so that their charge,  $\alpha P$ , is compensated for a fraction,  $(1 - \beta)$ , by a deficit of co-ions and a fraction,  $\beta$ , by an excess of counterions above the concentration  $c'_s$ , present outside the range of the electric field of the polyion. Thus:

$$c'_s = c_s + \alpha P c_p (1 - \beta) = c_s + \alpha c_m (1 - \beta). \quad (6)$$

$\beta$  approaches to 0.5 when  $c_s$  is high (say 1M) but is larger, up to about 0.9 for small  $c_s$  (and, of course, equal to 1 when no salt is present).

The Donnan pressure can then be written:

$$\pi_{Donnan} = c_m RT \left( \frac{1}{P} + \alpha \right) + (2c_s - 2c'_s) RT \quad (7)$$

where we have neglected the difference of the salt activity coefficients and unity. Using eqn (6) we have

$$\pi_{Donnan} = c_m RT \left( \frac{1}{P} + \alpha(2\beta - 1) \right) \quad (8)$$

which for high  $c_s$ , ( $\beta = 0.5$ ), approaches to

$$\pi_{Donnan} \approx c_m RT \cdot \frac{1}{P} \quad (9)$$

and shows that by using high concentrations of supporting electrolyte we may determine the degree of polymerization (and thus the molecular weight,  $M$ ) by osmotic measurements.

#### Light scattering

Light scattering may be considered to be due to the fluctuations in refractive index. In solutions these fluctuations are mostly due to fluctuations in concentration. In polyelectrolyte solutions the fluctuating entity is not the polyion, but an electroneutral region containing the polyion plus its surrounding ionic atmosphere, that is the polyion, the counterions, and a negative contribution from the expelled salt.<sup>24</sup> Vrij pointed out, that this salt expulsion has also to be taken into account in the value of  $dn/dc$ , the refractive index gradient. This can be done by determining the salt expulsion per unit charge of the polyion separately, or by measuring  $dn/dc$  in a Donnan equilibrium, in which the salt expulsion occurs spontaneously. This agrees with the fact that in the value of  $d\pi/dc$ , occurring in the light scattering equation,  $\pi$  is the Donnan pressure, because the fluctuations in polyion concentration take place in a salt containing medium, and not in pure solvent.

The strong repulsion between polyions leads to a high second virial coefficient and a relative decrease of the light scattering at higher concentrations. But with extrapolation to zero polyion concentration in the presence of a constant salt concentration ( $c_s = \text{constant}$ ) or salt activity ( $c'_s = \text{constant}$ ) and with the above mentioned precaution with respect to  $dn/dc$ , light scattering leads to correct values of the molecular weight of polyelectrolytes.

#### Titration of polyacids

In a titration of a polycarboxylic acid, such as polyacrylic acid or gum arabic, the dissociation constant, as conventionally defined, appears to decrease with increasing degree of neutralization,  $\alpha$ . This is easily explained, since with increasing negative charge of the polyion it becomes more and more difficult to dissociate a further hydrogen ion. The equilibrium equation therefore has to contain an extra term,  $\Delta G_{el}$ , which represents the increase in electrical free energy of the polyion and its atmosphere on increasing the polyion charge by one unit.

$$\text{pH} = \text{pK}_0 + \log \frac{\alpha}{1 - \alpha} + 0.43 \frac{\Delta G_{el}}{kT} \quad (10)$$

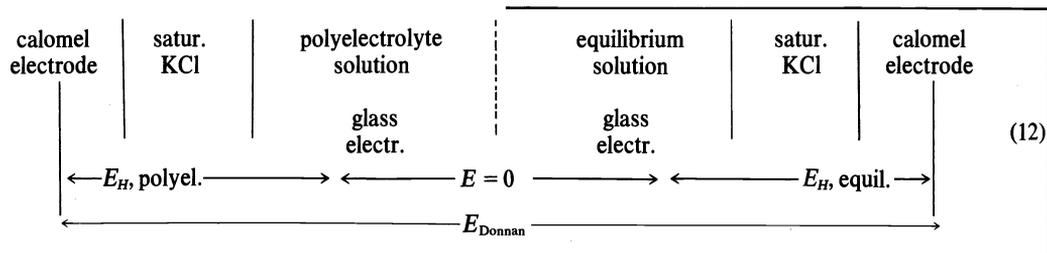
where  $\text{pK}_0$  is the intrinsic dissociation constant (at zero charge). Since  $\Delta G_{el}$  is expected to increase with  $\alpha$ , it is not

astonishing that Katchalsky and Spitnik<sup>25</sup> found that the titration data would often fit the empirical equation

$$\text{pH} = \text{pK}_0 + m \log \frac{\alpha}{1 - \alpha} \quad (11)$$

where  $m$  is a constant, larger than unity.

The theoretical calculation of  $\Delta G_{el}$  depends strongly on the model chosen for the polyion and is not easy.<sup>26</sup> Moreover, the matter is not quite as simple as it looks here, since it is questionable whether the pH calculated from the e.m.f. between a glass electrode and a calomel electrode with a saturated KCl salt bridge inserted in the polyelectrolyte solution is the correct value to be inserted in eqn (10).  $\Delta G_{el}$  is calculated assuming that the  $\text{H}^+$ -ions participating in the equilibrium come from a region with an electrical potential zero, but the salt bridge comes at some kind of an average potential in the solution and this is certainly more negative than a point far away from all the polyions. A good way to see whether this is a quantitatively important effect is to consider the titration cell as part of a Donnan system.<sup>27</sup>



$$E_{l,j} = -\frac{1}{F} \int_{\text{sat. KCl}}^{\text{solution}} \sum_i \frac{t_i d\mu_i}{Z_i} \quad (14)$$

In the equilibrium solution the  $\text{H}^+$ -ions are indeed far away from the polyions and may be considered to be at electrical potential zero. Therefore the pH in eqn (10) is the pH of the equilibrium solution, not that of the polyelectrolyte solution. Since the two glass electrodes are at the same potential (otherwise work could be extracted from a system in equilibrium) the two pH's differ by  $E_{\text{Donnan}}/59 \text{ mV}$ , or

$$\text{pH}_{\text{equil.}} = \text{pH}_{\text{polyel.}} - 0.43 \frac{FE_{\text{Donnan}}}{RT} \quad (13)$$

where  $E_{\text{Donnan}}$  has the same sign as the charge on the polyions.

The effect described in eqn (13) has been known since 1930 in soil science as the Pallmann and Wiegner effect.<sup>28</sup> It can be eliminated in polyacid titrations by extrapolating to polyion concentration zero, but keeping at least some low molecular weight salt present.

An old measurement<sup>29</sup> on the titration of gum arabic shows the influence of the concentration quite clearly (see Fig. 6).

*Activities of polyions, counterions and co-ions*

The mean activity coefficient,  $\gamma_{\pm}$ , for the polyion-counterion combination can be determined either from osmotic pressure data, using the Gibbs-Duhem relation, or directly (Dolar and Leskovšek<sup>30</sup>) using a galvanic cell with transference. In agreement with the fact that the osmotic coefficient is low, but fairly independent of the polyelectrolyte concentration,  $\log \gamma_{\pm}$  decreases strongly and linearly with the logarithm of this concentration.

Determinations of the single ion activities of the counterions and co-ions suffer from the same uncertainty as discussed above for the pH, viz. the uncertainty about the

liquid junction potential between the KCl bridge and the polyelectrolyte solution.

The product of the activities of the small ions, in which this uncertainty cancels, and which must be equal to the activity product for the ions in the Donnan outside solution, agrees well with the following data about the single ion activities.

Single co-ion activity coefficients are rather independent of the polymer concentration (Nagasawa, Izumi and Kagawa<sup>31</sup>) in agreement with the fact that they are pushed away from the polyions.

Counterion activity coefficients are low in saltfree polyelectrolytes and the activities are often found to be additive when salt is added, as shown particularly nicely by Mock and Marshall<sup>32</sup> for HCl added to polystyrenesulphonic acid.

Nevertheless, consider the role of the saltbridge in these measurements and the fact that the liquid junction potential,  $E_{l,j}$ , is given by

where  $t_i$ ,  $\mu_i$  and  $Z_i$  are the transference numbers, the chemical potential and the valence with sign included resp. of the ions  $i$ . Then it is obvious that the liquid junction potential not only depends on ion activities, but also on ion mobilities. As the mobilities are strongly affected by the presence of polyions (Overbeek<sup>27</sup>) it is amazing that such simple additivity laws should hold. We come back to this point later.

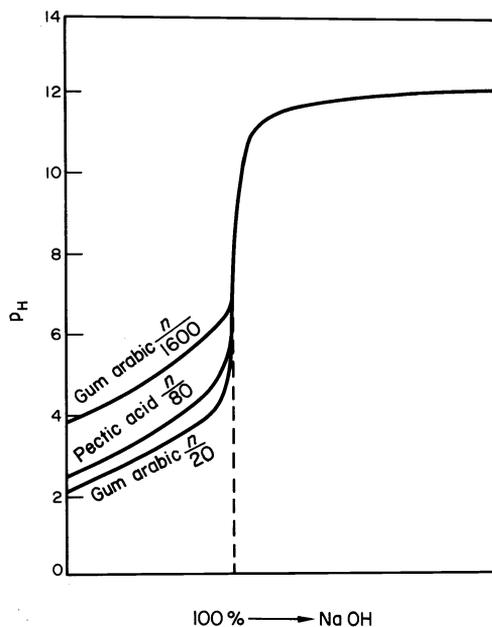


Fig. 6. Titration curves of gum arabic and of pectic acid.

### Swelling of polyelectrolyte coils and electroviscous effect

As mentioned in the introduction, the spectacular changes in viscosity caused by changes in charge density and salt concentration formed perhaps the most typical entry to polyelectrolyte research, and already at the Liège symposium in 1948, quantitative, although rather primitive theories of the electroviscous effect were given. Nevertheless, notwithstanding a great deal of effort from many sides the quantitative situation is still not satisfactory.

In the first place there are really three electroviscous effects, the classical, Smoluchowski's one, depending on distortion of the ionic atmosphere, the one caused by the swelling of individual coils, and one caused by the mutual repulsion between two polyions. The last one can be eliminated by dilution of the polyelectrolyte, but this has to be done at constant activity of the small ions, in order to keep the average conformation of the polyion independent of its concentration. Isoionic dilution (keeping the total number of small ions constant) has been introduced<sup>33</sup> to achieve this aim at least approximately. Dilution in a Donnan equilibrium with the outside solution kept constant would be still better.

Furthermore the relation between (intrinsic) viscosity and shape of the coil is not at all simple. Semi-empirical equations are used here, derived from work on non ionic polymers and one of the stumbling-blocks is the uncertainty about the friction constant of individual chain elements or of a given length of the chain. We shall later encounter the same difficulty in the interpretation of electrophoresis.

Finally the problem of minimizing the total free energy of the coil, consisting of the electrical free energy of its charges and their ionic atmospheres and of the configurational free energy has not yet received a completely satisfactory answer.

There are other ways of obtaining information on the coil expansion. The best one probably is to use the angular dependence of the light scattering with a Zimm-plot as worked out by Orofino and Flory.<sup>34</sup> Another is studying the swelling of lightly cross linked gels (Katchalsky, Lifson and Eisenberg<sup>35</sup>).

Kuhn and Katchalsky and coworkers<sup>36</sup> drew attention to the possibility of deriving mechanical work from the changes in volume of polyelectrolyte gels and coined the term "mechanochemistry". Since living organisms can convert chemical into mechanical energy, it is tempting to look for a possible relation with the changes in size of polyions.

Finally we should mention that in heavily crosslinked polyelectrolytes, used as ion exchangers, on the one hand swelling and shrinking is a nuisance, but on the other hand the high concentration of charges and therefore of counterions may give possibilities for specific differences between ions of the same valence, say K vs Na.<sup>37</sup>

### Protective action and sensitization

Amongst one of the oldest applications of polyelectrolytes is their use as protective agents. When the surfaces of hydrophobic particles or emulsion droplets are fully covered by an adsorbed layer of polyelectrolyte, these particles become very resistant against flocculation, because now their surface layers are compatible with water. As a matter of fact important natural emulsions, such as milk and latex, are protected in this way by adsorbed proteins.

Only later it was discovered that very small concentra-

tions of protective agents may act as sensitizers by the fact that under such circumstances one polyion may get adsorbed on two particles and thus bind them together. Sensitization has obtained a new importance in the protection of the environment because it may be used as a method for precipitating otherwise persistent suspensions. One example is the cleaning of effluents of coal washeries.<sup>38</sup>

The mechanism of protection as such is fairly well understood. Loosely protruding chains behave nearly as free molecules and when the protruding ends of the chains adsorbed on two different particles come close together, both the local increase in concentration and the loss of conformational freedom represent an increase in the free energy of the system and thus lead to repulsion. See Hesselink and others.<sup>39</sup>

The quantitative description of the adsorption and especially the influence of small ions on it still leaves something to be desired. Moreover the mutual repulsion of polyelectrolytes is more complex than that of uncharged polymers, treated in the above mentioned theories.

### Transport phenomena, in particular electrophoresis

Having discussed viscosity earlier, the main remaining transport phenomena are sedimentation, diffusion and electrical conductance and electrophoresis. We shall concentrate our attention to the transport in an electric field.

Experimentally it is found that electric transport is nearly independent of molecular weight; the co-ions have about the same mobility that they have in the absence of polyelectrolyte; the mobility of the counterions is quite low and in some cases even negative. The mobility of the polyions increases less than proportionally with charge density, and generally decreases with increasing ionic strength. An exception has been reported by Nagasawa *et al.*<sup>40</sup> at very low ionic strength.

Theoretically one expects the electrical transport to be determined by the ideal mobilities of polyion and small ions, as modified by the electrophoretic retardation (hydrodynamic interaction between polyion and small ions), the relaxation effect (distortion of the ionic atmosphere) and possibly by binding between polyion and small ions.

There are several more or less complete theories for the electrophoretic retardation, in which the polyion is either treated as a porous sphere, or as a randomly kinked cylinder, but the theories for the relaxation effect (Longworth and Hermans,<sup>41</sup> Imai and Iwasa<sup>42</sup>) are still in development and not easily applicable. With the aid, however, of the semiempirical method introduced by Möller, van Os and Overbeek<sup>43</sup> the effect of the distortion of the ionic atmosphere can be eliminated and then theories, which only take the electrophoretic retardation into account, can be used. The method of Möller *et al.* is based upon the idea, that the ionic atmosphere, either resting or distorted depends little on the kind of counterions (only on their valence), and further that the relaxation effect is due to an electrical interaction between the polyion and its atmosphere and thus can be represented by an average electric field acting on polyion and on its counterions and slowing them all down in the same proportion.

This being the case the electrophoretic mobility of the polyion can be written as

$$U_p = (U_p^0 - U_{p,er})(1 - \Delta X/X) \quad (15)$$

and the mobility of the counterions as

$$U_c = (U_c^0 - U_{c,er})(1 - \Delta X/X) \quad (16)$$

where  $U_p^0$  and  $U_c^0$  represent the ideal mobilities of polyion and counterion resp.,  $U_{p,er}$  and  $U_{c,er}$  the respective electrophoretic retardations,  $X$  the applied field strength and  $\Delta X$  the average relaxation field. Since the distribution of counterions is assumed to be independent of their nature (at constant valence),  $U_{c,er}$  is also independent of it. Therefore for two different counterions, say 1 and 2, we obtain two eqns (16) from which  $U_{c,er}$  can be eliminated leading to

$$1 - \Delta X/X = \frac{U_1 - U_2}{U_1^0 - U_2^0} \quad (17)$$

or, introducing equivalent conductancies,  $\lambda = FU$ , we have

$$1 - \Delta X/X = \frac{\lambda_1 - \lambda_2}{\lambda_1^0 - \lambda_2^0} \quad (18)$$

The mobility and the equivalent conductance of the polyion are also independent of the kind of counterion and so  $\lambda_1 - \lambda_2 = \lambda_{p1} - \lambda_{p2}$  where  $\lambda_{pi}$  represents the equivalent conductance of the polyelectrolyte with its counterions of type  $i$ . Consequently

$$1 - \Delta X/X = \frac{\lambda_{p1} - \lambda_{p2}}{\lambda_1^0 - \lambda_2^0} \quad (19)$$

This equation can not only be applied to salt free polyelectrolytes but also to the increase of the conductance of a salt solution, caused by the addition of polyelectrolyte. Equation (19) has been tested recently by Van der Drift<sup>44</sup> by determining the conductance of LiPMA, NaPMA and KPMA (salts of polymethacrylic acid) at different degrees of neutralization,  $\alpha$ , and in the presence of different concentrations of the corresponding bromide. If eqn (19) is rewritten as

$$\lambda_{p1} = \lambda_{p2} - \lambda_2^0(1 - \Delta X/X) + \lambda_1^0(1 - \Delta X/X) \quad (20)$$

it is clear that straight lines with a slope  $(1 - \Delta X/X)$  are expected when  $\lambda_{p1}$  is plotted against  $\lambda_1^0$ . Figure 7 shows that this is indeed the case. The values of  $(1 - \Delta X/X)$  are collected in Table 1 and are seen to be on the order of 0.5.

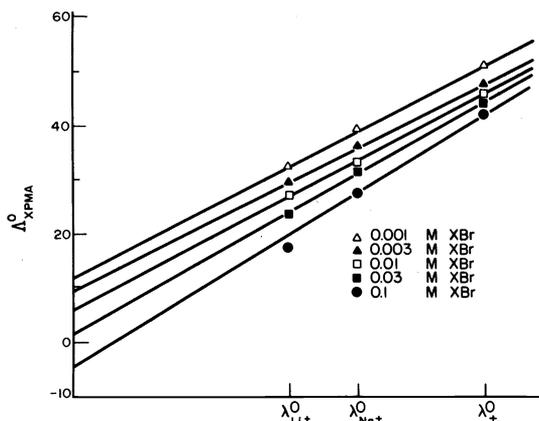


Fig. 7. Equivalent conductance of XPMA at  $\alpha = 0.5$  (polymethacrylic acid, half neutralized with XOH, X being Li, Na or K) against the corresponding equivalent conductance at infinite dilution of X in solutions of XBr. Equivalent conductances in  $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ .

Table 1. Values of  $(1 - \Delta X/X)$  at different degrees of neutralization,  $\alpha$ , and at different bromide concentrations,  $c$

| $\alpha$ | $c(\text{mol/l})$ |       |      |      |      |
|----------|-------------------|-------|------|------|------|
|          | 0.001             | 0.003 | 0.01 | 0.03 | 0.1  |
| 0.3      |                   | 0.54  | 0.56 |      | 0.54 |
| 0.5      | 0.52              | 0.52  | 0.54 | 0.57 | 0.63 |
| 0.7      |                   | 0.42  | 0.45 |      | 0.62 |

By using Hittorf transference measurements, Van der Drift<sup>44</sup> determined electrophoretic mobilities of the polyions and mobilities of co- and counter-ions. The mobilities of the co-ions decreased slightly with increasing polyelectrolyte concentration, the cation mobilities were low and sometimes negative, due to the combination of electrophoretic retardation and relaxation effect, the polyion mobilities decreased strongly with increasing ionic strength, were independent of the polymer concentration and increased only slowly with the degree of dissociation, as shown in Figs. 8–10 and in Tables 2 and 3.

Electrophoretic mobilities, corrected for relaxation by dividing them by  $(1 - \Delta X/X)$ , can now be compared with the different theories. However, whatever model is chosen, the friction constant per unit length of the molecule remains an adaptable parameter in any model. We come back to this interpretation in a later section.

The fact that the r.h.s. of eqn (19) is independent of the choice of the counterions has been signalled by Eisenberg<sup>46</sup> and has been interpreted on the simple basis that a fraction,  $(1 - f)$ , of the counterions is bound to the polyion and moves along with it (cf. Huizinga, Grieger and Wall<sup>47</sup>). Manning<sup>48</sup> indicates still another interpretation of the same quantity,  $f$ , viz. as the ratio of the self-diffusion coefficient of the counterions in the (salt-free) polyelectrolyte solution to that of the free ions, but in these interpretations the total conductance of the polyelectrolyte salt is given as  $\lambda_{p1} = f(\lambda_1^0 + \lambda_p)$ , whereas in the one given above it is  $\lambda_{p1} = (1 - \Delta X/X)(\lambda_1^0 - \lambda_{1,er}) + \lambda_p$ .

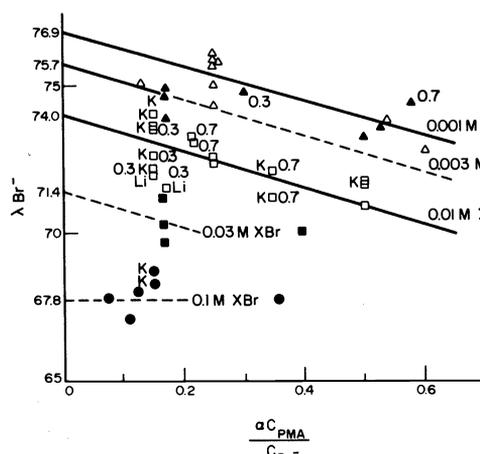


Fig. 8. Influence of the PMA concentration on the equivalent conductance of the bromide ions at  $\alpha = 0.3$ ,  $\alpha = 0.5$  and  $\alpha = 0.7$  with Li, Na or K as counterions. Symbols are marked 0.3, 0.5, Li or K for experiments at  $\alpha = 0.3$ ,  $\alpha = 0.5$ , Li or K as counterions. Symbols are not marked for  $\alpha = 0.5$  and for Na as counterions.  $\alpha C_{PMA}$  = concentration of ionized  $\text{COO}^-$ -groups in equiv/l.  $C_{Br^-}$  = concentration of bromide ions in equiv/l.  $\lambda_{Br^-}$  in  $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ .

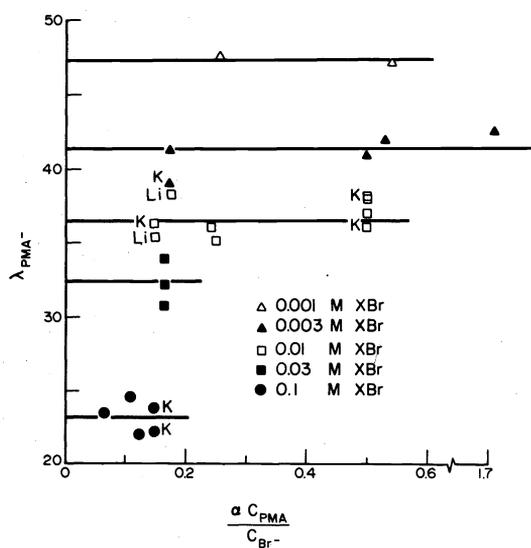


Fig. 9. Equivalent conductance in  $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$  of polyion,  $\lambda_{\text{PMA}^-}$ , at  $\alpha = 0.5$  plotted against  $\alpha C_{\text{PMA}^-}/C_{\text{Br}^-}$ . Unmarked symbols refer to Na counterions.

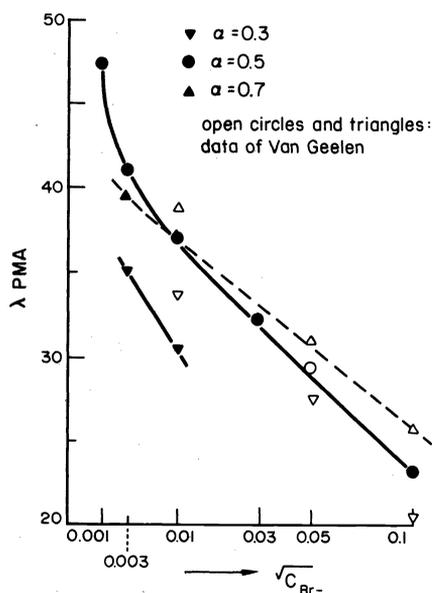


Fig. 10. Equivalent conductance in  $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$  of polyion plotted against  $(C_{\text{Br}^-})^{1/2} \cdot C_{\text{Br}^-}$  in eq/l.

Manning also assumes that  $\lambda_{1,cr}$  is negligibly small. In order to choose between the different interpretations it would be very important to have a complete theory for the relaxation effect, which is now only available for a massive sphere, but not for a porous sphere or a kinked cylinder.

#### Dielectric properties of polyelectrolyte solutions

The polarization of the ionic atmosphere in an electric field does not only manifest itself as the relaxation effect in electrophoresis, but also in an increased static dielectric constant, with dispersion at higher frequencies. It is interesting to note that already in 1922 Errera<sup>49</sup> discovered that aged sols of vanadium pentoxide, which contain very long particles, had an excessively high dielectric constant; a sol containing only 1% of vanadium pentoxide had a static dielectric constant of 400. We may mention

Table 2. Equivalent conductance in  $\text{ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$  of the polyions at 25°C. Values in italics determined by Van Geelen<sup>45</sup> (1958) at 5°C in NaCl solutions and multiplied by  $\eta_{5^\circ}/\eta_{25^\circ} = 1.70$

| $\alpha$ | XBr (mol/l) |       |      |      |      |      |      |      |      |      |
|----------|-------------|-------|------|------|------|------|------|------|------|------|
|          | 0.001       | 0.003 | 0.01 | 0.03 | 0.05 | 0.1  |      |      |      |      |
|          | Na          | K     | Na   | K    | Na   | K    |      |      |      |      |
| 0.1      |             |       | 27.0 |      | 18.4 | 13.9 |      |      |      |      |
| 0.2      |             |       | 28.7 |      |      |      |      |      |      |      |
| 0.3      |             | 35    | 30.6 | 30.2 |      |      |      |      |      |      |
|          |             |       | 33.8 |      | 26.9 | 20.4 |      |      |      |      |
| 0.5      | 47          | 48    | 41.3 | 39   | 36.2 | 36.0 | 36.4 | 32.3 | 29.6 | 23.5 |
| 0.7      |             |       | 39.5 |      | 37.0 | 37.0 | 37.2 |      | 30.9 | 25.8 |
|          |             |       |      |      | 38.8 |      |      |      | 31.6 | 26.9 |
| 0.9      |             |       |      |      | 39.4 |      |      |      |      |      |

Table 3. Equivalent conductance in  $\text{ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$  of the counterions that compensate the charge of the polyions

| $\alpha$ | XBr (mol/l) |       |      |      |     |    |    |   |    |    |
|----------|-------------|-------|------|------|-----|----|----|---|----|----|
|          | 0.001       | 0.003 | 0.01 | 0.03 | 0.1 |    |    |   |    |    |
|          | Na          | K     | Na   | K    | Li  | Na |    |   |    |    |
| 0.3      |             |       | 15   |      | 15  | 27 |    |   |    |    |
| 0.5      | -2          | 9     | 1    | 15   | -3  | 3  | 15 | 5 | 10 | 25 |
| 0.7      |             |       | -5   |      |     | -6 | 6  |   | 5  |    |

the pioneering work of Oncley<sup>50</sup> on proteins, and that of O'Konski<sup>51</sup> on a direct determination of relaxation times. More recent work has been done by Mandel<sup>52</sup> and coworkers, by Sachs *et al.*<sup>53</sup> and by Oosawa.<sup>54</sup> From a paper by Mandel and Van der Touw<sup>55</sup> we reproduce Fig. 11, showing the dispersion of the dielectric constant of DNA-solutions. There are two dispersion regions one at high ( $10^6$ – $10^7$  Hz) and one at low frequency ( $10^3$  Hz and lower). The dielectric increment through the high frequency dispersion region is largely independent of molecular weight and even of the kind of polyelectrolyte, but the low frequency increment increases with molecular weight. The authors propose a semi-quantitative explanation in which both effects are due to polarization of the atmosphere parallel to the chain, the high frequency effect being due to displacements along relatively short (say 500 Å), relatively straight parts of the chain, the low frequency effect including displacements along the whole chain.

#### Theoretical considerations based on different models

For the theoretical treatment of polyelectrolyte properties three models have been mainly used, that of a chain of individual charges, each surrounded by its own atmosphere, that of the porous sphere and that of the coiled cylinder, the last one often approximated as a line charge. The chain model with individual charges and atmospheres is difficult to handle in detail. In the porous sphere model, the elements of the polyion and its charges are assumed to be more or less uniformly distributed in a spherical volume and the atmospheric countercharge is also assumed to be smeared out inside and outside that sphere. To be acceptable, such a model requires that the Debye-Hückel length (thickness parameter of the atmosphere) is not only large compared to the average distance between neighbouring charges on the polyion (which is often the

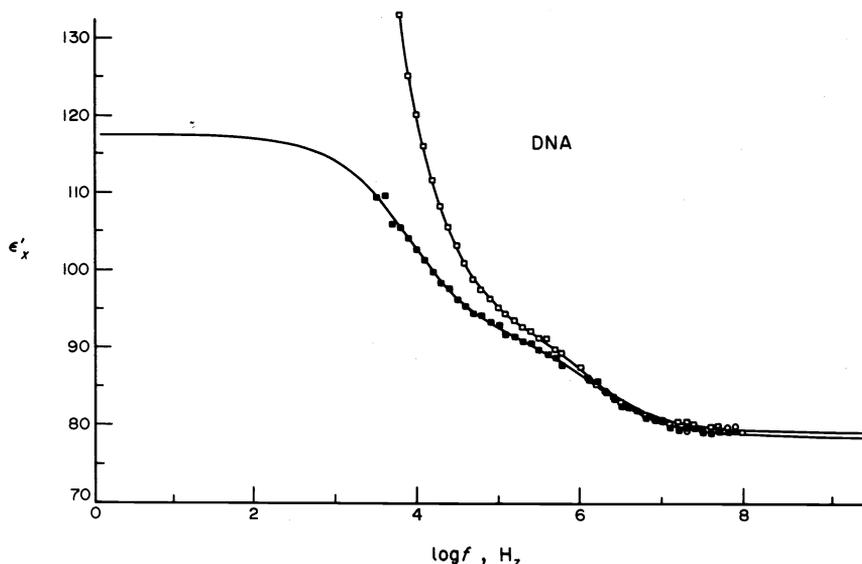


Fig. 11. Electric permittivity,  $\epsilon'_x$ , (dielectric constant) against the frequency,  $f$ , in Hertz for NaDNA of two different degrees of polymerization,  $P$ . Concentration of NaDNA =  $10^{-3}$  eq/l;  $\alpha \sim 1$ ;  $\blacksquare$ :  $P = 1200$ ;  $\square$ :  $P = 18,000$ .

case) but also with respect to the average distance between more distant parts of one coiled polyion. Due to the open nature of the polyion coil this last condition is rarely met (coil size as derived from light scattering, sedimentation, viscosity or purely theoretical calculation) and consequently the cylinder model (or line charge) is to be preferred, as has been repeatedly emphasized by several authors.

In one case, however, a model with a continuous distribution of polyion charges and of the small ions through a macroscopic volume has been successful. That case is the explanation of complex-coacervation by Voorn and Overbeek<sup>56</sup> and by these same authors with Michaeli.<sup>57</sup> The electrical free energy of that system can be reasonably approximated as a collection of Debye and Hückel atmospheres. But in this case, of course, the concentration of the polyions is quite high, and their mutual distance small compared with the Debye and Hückel length.

In explaining the swelling of individual coils by increased electric charge or decreased electrolyte content, the porous sphere model at first sight looks more attractive than the cylinder model, because in the cylinder model interactions between distant parts of the chain are small and often negligible. But since the porous sphere model as such is usually not acceptable, we have to try to interpret the swelling of the coil in terms of the cylinder model. The uncoiling effect of charge and low salt content must then be due to relatively short range effects, i.e. to stretching local parts of the chain under decrease of the free energy, which thus makes the chain stiffer and more open. Oosawa<sup>58</sup> discussed this situation also from the thermodynamic side, but a quantitative theory based on this uncoiling effect is still lacking.

In discussing the distribution of small ions around a cylindrical polyion, the free energy of the ionic atmosphere and the osmotic and activity effects based on it, the notion of counterion condensation has played an important role. The necessity of counterion condensation has been most clearly emphasized by Manning,<sup>59</sup> who approximates the cylinder with its charges as a line charge with a linear charge density such that one elementary charge

occurs per length,  $b$ . Then the situation of the countercharge becomes unstable when—for monovalent counterions—the parameter  $\xi$  becomes larger than one. So

$$\frac{e^2}{\epsilon k T b} = \xi \leq 1 \quad (21)$$

where  $e$  is the elementary charge,  $\epsilon$  the dielectric constant of the medium, and  $k$  and  $T$  the Boltzmann constant and the temperature, respectively. Any counterions leading to an excess of  $\xi$  over 1 will have to condense on the polyion. This approach leads to limiting laws for systems of infinitely long line charges and point ions in the limit of infinite dilution, but Manning shows, how well these limiting laws apply also to finite concentrations and in the presence of salts.

The limiting laws give good values for the osmotic coefficient,  $\gamma_p$ , are in agreement with the additivity of osmotic pressures, (eqn 5), predict the salt expulsion (eqn 6) and the oncotic pressure in the Donnan equilibrium, and lead to values for the activity coefficients of the small ions and of the polyions, but they contradict the additivity of counterion activities. The application to self-diffusion and electrical transport was mentioned above.<sup>48</sup> It is no exaggeration to consider the limiting laws the most important development in polyelectrolyte theory of the last decade.

Nevertheless, the actual polyion is not a line but has a finite cross-section, the ions are not point charges, and for realistic diameters and in the presence of not too small salt concentrations ( $> 0.001$  M) the Poisson-Boltzmann equation around a cylinder can be solved without running into infinities (Philip and Wooding<sup>60</sup>). Van der Drift<sup>44</sup> used these solutions, combined them with Henry's solution<sup>61</sup> for the electrophoresis of cylinders and Möller's *et al.*<sup>43</sup> method for eliminating the relaxation effect and could explain his results for the electrophoresis of PMA with very reasonable assumptions for the radius of the solvated cylinder (3.5–8 Å, increasing with charge density) and the solvated counterions (3.5 Å for alkali-ions). Only for electrolyte contents of 0.1 M he had to assume a partial interpenetration of the solvation layers.

### Gaps in our understanding of polyelectrolytes: future developments

At the present moment the main features of polyelectrolyte solutions, both saltfree and in the presence of low molecular weight salts are well understood, and the quantitative agreement between theory and experiments is reasonable, often quite good. Nevertheless there are still a number of gaps in our understanding.

The present theories on Donnan potentials and on the activity of counterions use contradictory assumptions about the liquid junction potential and still have to be reconciled.

The "additivity rule" for counterion activity finds no simple foundation in the existing theoretical structure and is at variance with the limiting laws (Manning<sup>62</sup>). Nevertheless, the additivity rule has often been found to be approximately true. This situation deserves further clearing up. In this respect it is highly desirable to extend the treatment, that has led to the limiting laws, to finite radii of the cylinders and ions, to finite concentrations, and to higher approximations to the solution of the Poisson-Boltzmann equation, in order to obtain a better estimate of the range of validity of this treatment.

An *a priori* theory of the relaxation effect for cylinders is dearly needed for the full interpretation of electrophoresis and conductance.

A more complete quantitative theory of swelling of the polyion coil based on the cylinder model is desirable, as is its application to viscosity and sedimentation.

It might repay to reconsider the specific ion effects, found by Bungenberg de Jong<sup>63</sup> and mentioned above, especially with regard to the possible application of ion exchangers or ion exchange membranes to the elimination of certain ions from waste liquors, or in concentrating dilute sources of ions.

More extensive and better directed application of polyelectrolytes in protective action and sensitization requires in the first place a better understanding of the adsorption of polyions at interfaces and how it is affected by the presence of small ions.

Wider application of polyelectrolyte knowledge in biochemistry is well worth promoting. Not so much because polyelectrolyte properties in themselves will explain the behavior of living systems, but because they are a factor in many phenomena, such as the interaction between nucleic acids and basic proteins, or the change in conformation of muscle and other proteins. Even memory might be connected with hysteresis as pointed out clearly by Aharon Katzir-Katchalsky.<sup>64</sup>

In summary, polyelectrolyte science is very much alive, with a solid basis of knowledge, and still lots of work to do.

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