INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROANALYTICAL CHEMISTRY*
AND COMMISSION ON EQUILIBRIUM DATA†

CONDUCTOMETRIC ANALYSIS OF POLYELECTROLYTES IN SOLUTION

Prepared for publication by
HERMAN P. VAN LEEUWEN[1], ROB F. M. J. CLEVEN[2]
and PAVEL VALENTA[3]

[1]Wageningen Agricultural University, Dreijenplein 6, 6703 HB Wageningen, Netherlands
[2]National Institute of Public Health & Environmental Protection, POB 1, 3720 BA Bilthoven, Netherlands
[3]Institute of Applied Physical Chemistry, KFA, POB 1913, D-5170 Jülich, FRG

Conductometric analysis of polyelectrolytes in solution

Abstract - Theoretical developments concerning ion association phenomena and their implications for conductivities of polyelectrolyte solutions are surveyed. Attention is focused on the characteristics of polyion/counterion association and conductivities of polyionic species. The existing literature on experimental studies of model systems is critically reviewed. Central issue is the analysis of counterion distribution, which may be quite typical in a certain range of polyionic charge densities. Simultaneously occurring intrinsic binding between polyion and counterion is taken into consideration. The rather extensive literature on conductometric protolytic titration of polyacids and polybases is reconsidered. Many conductometric titration curves for natural polyelectrolytes such as humic acids have originally been interpreted in terms of different types of functional groups. The present report shows that such interpretation is at least premature since the data are equally well explained by counterion association, as imposed by the polyionic charge densities involved. By utilizing the effects of counterion association (especially those of higher-valency ions), conductometry can be fruitfully applied in the quantitative analysis of charged groups on polyelectrolytes.

I. INTRODUCTION

Conductometry continues to be an important tool in the analysis of the physico-chemical properties of polyelectrolyte solutions. Since the review by *Kurucsev* and *Steel* [1], emphasizing the phenomenology of counterion association, substantial progress has been made in:

(i) development of the theory of polyelectrolytes, in particular with respect to counterion binding, and the elaboration to conductivity characteristics;

(ii) acquisition of accurate pertaining experimental data under a variety of conditions.

The recent developments shed new light on such problems as the dependence of the overall conductivity of a polyelectrolyte solution on the concentration, and its dependence on the nature of the counterion. On a more practical level, the typical phenomena of association between polyion and counterions have been fruitfully utilized for analytical purposes. For example, the conductometric titration of weak polyacids yields well-defined end-points, especially if hydroxides of higher valency metals are employed. Thus, at not too high salt levels, the conductometric titration compares quite favourably with the potentiometric one. For natural samples analogous results have been presented. Interpretation of the titration curves can be improved with the recent theoretical results. More direct use of measured conductivities is made in metal speciation studies. It has been shown to be possible to estimate the distribution of the counterions (over free and bound states) by variation of the nature of the counterion. The procedure can also be applied to mixtures of counterions, even if different valencies are involved. This allows the utilization of conductometry in the speciation of divalent (e.g., heavy) metals in polyelectrolyte systems at finite 1:1 salt levels.

The present report is intended to:

(i) summarize and evaluate the developments in the theories for association phenomena in polyelectrolyte systems;

(ii) derive the implications for the distribution of ions in polyelectrolyte solutions, and the ensuing conductivities;

(iii) critically review the existing literature on conductometric analysis of polyelectrolytes;

(iv) indicate how polyion-counterion interactions can be successfully utilized in conductometric analysis of polyelectrolytes.

II. THEORY

Phenomenological formulation

A suitable starting-point [1] is the *formal* expression for the molar conductivity Λ (see Note) of a pure polyelectrolyte solution (no salt added) i.e., a solution containing only polyions p and counterions:

$$\Lambda = f(\lambda_c + \lambda_p) \tag{1}$$

where λ_c and λ_p represent the ionic conductivities of the counterions and the polyions, respectively, and f is some fractional parameter which is *related* to the fraction of *free* counterions. To consider f as identical to the fraction of free ions would reduce the

gradually changing degree of interaction between polyion and counterion to a *two-state* approximation: a fraction f being completely free and a fraction $(1-f)$ being fully bound. In reality *all* counterions are in interaction with the polyions to some extent. Some are *condensed*, i.e., electrostatically trapped by the highly charged polyion, others are constituents of the diffuse countercharge and located at some distance from the polyion.

Equation (1) can be developed to an expression in which λ_c is replaced by λ_c°, the counterion conductivity in pure solvent [2,3,4]:

$$\Lambda = f(\lambda_c^\circ + \lambda_p) \tag{2}$$

The important difference as compared to eq. (1) is that with known (tabulated) values of λ_c° experimental values of Λ can be analysed into f and λ_p. This aspect will be further developed later on.

Let us first consider solutions that not only contain a polyion and its counterions but also a simple salt. Then, a different book-keeping of the counterions with respect to the polyionic charge has to be considered and the co-ions have to be taken into account as well. Studies, to be discussed below (as e.g., summarized in the reviews by *Overbeek* [5] and *Mandel* [6], suggest that the co-ions may usually be considered to behave independently with respect to the polyions. This implies that the linear dependence of Λ on λ_c° is maintained and that eq. (2) may be generalized. Let us, for the sake of convenience, consider a negatively charged polyion p^{z-}, so that in principle *all* cations in the system are (potential) counterions of p^{z-} and all anions are co-ions. The essential difference between counterions and co-ions is that counterions not only are constituents of the diffuse countercharge around the polyion, but may also be trapped (condensed) by the polyionic charge, whereas co-ions are only involved as constituents of the diffuse countercharge atmosphere. Thus, in terms of the conductivity κ, eq. (2) may be generalized to:

$$\kappa = \sum_i z_i f_i \lambda_i^\circ c_i + \sum_j z_j \lambda_j c_j + n f_p \lambda_p c_p \tag{3}$$

where:
- the indices i and j refer to counterions and co-ions, respectively;
- c denotes the analytical concentration, and c_p refers to the *charged groups* on the polyion. For example for *n*-valent groups we have $c_p = \frac{z}{n}[p^{z-}]$;
- λ_i°, λ_j and λ_p are the ionic conductivities of counterions i in pure solvent, of co-ions j and of the polyion, respectively;
- f_i is the distribution parameter of counterions i, and f_p the charge fraction of the polyion respectively.

It is sometimes convenient to use the degree of coverage θ_i, the number of apparently bound countercharges per charged *group* on the polyion, defined as:

$$\theta_i = \frac{(1 - f_i)c_i}{c_p} \tag{4}$$

$$f_p = 1 - \frac{1}{n}\sum_i z_i \theta_i \tag{5}$$

At first glance, the formulation of eq. (3) suggests that only free groups or ions contribute to the conductivity, i.e., that the association of a negative group on the polyion with a positive counterion of the same valence would result in the complete loss of their conductivities. It is tempting to derive such physical significance from the scheme but, so far, it is only a way of book-keeping in which all the ignorance concerning the mechanism of conduction by polyionic segments is hidden in f_i and λ_p (effects on λ_j usually being negligible).

For analytical purposes it is often necessary to obtain information on the values of both f and λ_p. Either one wants to collect data on c_p, and has to take into account the influence of the counterions on f and λ_p, or one would like to measure counterion distribution and needs to know λ_p. In all cases, knowledge of the behavior of f_i is mandatory for a proper handling of θ_i and λ_p. This leads us to the root of the difficulties with conductometry of polyelectrolytic systems: to separate the charge distribution parameter f and the conductivity of the polyion λ_p. *Eisenberg* [7] first tackled the problem by varying the value of λ_c° in a salt-free polyelectrolyte solution (no co-ions). The idea is that the extent of binding does not depend on the nature of the counterion, so that eq. (2) would be applicable. The approximation is reasonable in the case of purely

---

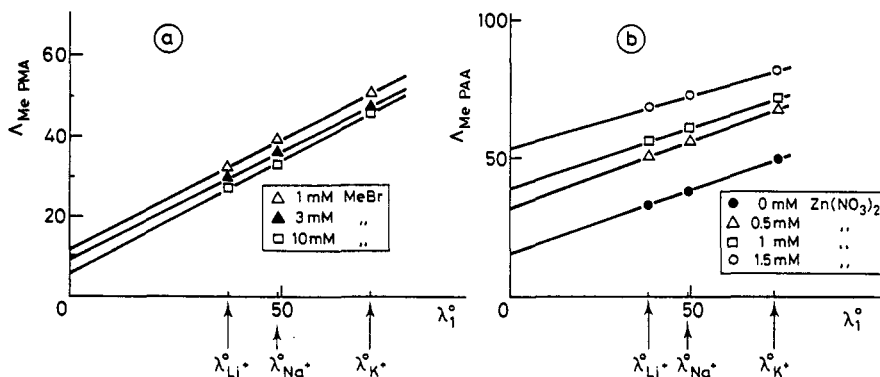Note: A list of symbols and abbreviations is given at the end.

Fig. 1. Conductivities of polyelectrolyte solutions as a function of individual counterionic conductivities for various concentrations of: a. co-ions and b. competing divalent counterions. From refs. [8] and [9]. Λ and λ in $S.mol^{-1}.cm^2$.

a. MePMA (Me—Li^+, Na^+, K^+), α_n=0.5, various [MeBr].

b. MePAA (Me—Li^+, Na^+, K^+), α_n=0.8, various [$Zn(NO_3)_2$].

electrostatic interaction, i.e., in the absence of ion-specific chemical contribution to the polyion-counterion association. The usefulness of this approach has already been shown in a number of experimental studies. For example, van der Drift [8] and Overbeek [5] obtained perfectly linear relations between Λ and λ_c° for Li-, Na- and K-polymethacrylate solutions at the millimolar level. Thus they found:

$$\frac{\Lambda_{KPMA} - \Lambda_{NaPMA}}{\lambda_K^\circ - \lambda_{Na}^\circ} = \frac{\Lambda_{KPMA} - \Lambda_{LiPMA}}{\lambda_K^\circ - \lambda_{Li}^\circ} = \frac{\Lambda_{NaPMA} - \Lambda_{LiPMA}}{\lambda_{Na}^\circ - \lambda_{Li}^\circ} \qquad (6)$$

which - according to eq. (2) - is identical to f_+, the distribution parameter for monovalent counterions. Not less interesting is their finding that the linear relationship is retained in the presence of (bromide) co-ions (see Fig. 1a). In line with this, de Jong et al. [9] showed that for Li-, Na- and K-polyacrylate systems, the purely electrostatically interacting counterions also behave identically in their competition with other counterions like Zn^{2+} (see Fig. 1b). All this verifies eq. (2) and to some extent eq. (3). Thus, the intercepts and slopes of the Λ, λ_c°-plots yield values for f_i and λ_p. In section III we shall discuss various results. It is not uncommon to speak about f in the simple terms of the fraction of free, unbound ions. However, as stressed before, one could equally well (or maybe better) decide to interpret the loss of conductivity in terms of the relaxation effect [5]. This effect originally refers to the retardation caused by the asymmetry of the charge distribution around each ion in an external electrical field.

Another option is to formally relate the loss of conductivity with a reduction of the average self-diffusion coefficient (D) of the counterions as compared to that in the polyelectrolyte-free solution (D°) [4], according to:

$$f = \frac{D}{D^\circ} \qquad (7)$$

At this point, we shall discuss some theoretical approaches to λ_p (and f) in some detail.

Theories of λ_p

The theoretical background of λ_p and f strongly varies with the particular type of polyelectrolyte involved. In one extreme (that is, in the limit of a -porous- sphere without drainage) the electric mobility u_p of a polyion is basically determined by the hydrodynamic properties of a compact macromolecular entity as a whole. In another extreme it is the mobility of the individual charged segment which determines the effective rate of migration in an applied field. In all cases, accounting for the countercharge distribution calls for some model and distinct approximations.

The porous sphere model. In the case of a coiled polyion, the conductivity is a complex property since small ions (mainly counterions, but co-ions are not necessarily absent) penetrate the coil. To a certain extent, these ions are trapped within the polyionic field and their contribution to the conductivity is correspondingly reduced.

If the segment density within the coil is so high that there is negligible drainage of the coil, then the mobility of the polyelectrolytic entity is primarily determined by a classical Stokes-type of friction coefficient $6\pi\eta a_s$ (where η is the medium

viscosity and a_s the radius of the 'particle' that is supposed to be spherical). The migration in an external field is extensively described in the colloid chemical literature on the electrophoresis of charged spheres. According to *Henry* [10] the electrical mobility u_p of an isolated spherical charged particle is given by:

$$u_p = F(\kappa_D a_s) \frac{\epsilon \epsilon_o \zeta}{\eta} \tag{8}$$

where the function $F(\kappa_D a_s)$ has the limits:

$$F(\kappa_D a_s) \longrightarrow 1 \qquad \text{for } \kappa_D a_s \longrightarrow \infty \tag{9a}$$

$$F(\kappa_D a_s) \longrightarrow \tfrac{2}{3} \qquad \text{for } \kappa_D a_s \longrightarrow 0 \tag{9b}$$

and with ζ being the electrokinetic or zèta potential, η the viscosity of the medium and κ_D the reciprocal *Debye* screening length. For a symmetrical z-z electrolyte at a concentration c, (counterions i, co-ions j) κ_D is given by:

$$\kappa_D^2 = \frac{F^2}{\epsilon \epsilon_o RT} \sum_{i,j} c_{i,j} z_{i,j}^2 \tag{10}$$

Using eq. (8), the electrical parameter ζ will lead to the charge of the particle. In this particular case, the charge σ is some net result of the structural polyionic charge and the counterions/co-ions contained within the sphere or, more accurately, within the sphere and the shell of liquid between the particle surface and the shear plane. For the present spherical geometry, the *Poisson-Boltzmann* equation can be solved, yielding for low potentials with neglection of the distance between shear plane and surface with respect to a_s:

$$\sigma = \epsilon \epsilon_o \frac{1 + \ell_D a_s}{a_s} \zeta \tag{11}$$

More generally, for potentials not well below RT/F, it is necessary to evaluate the charge σ from the measured ζ by numerical calculation or by interpolation using tables [11]. Though sufficiently laborious, the eventual result gives an idea how many counterions are confined to the polyionic sphere. The treatment is still approximate in that it ignores the relaxation effect on u_p. In this respect it is noteworthy that in the range $10^{-1} < \kappa_D a_s < 10^2$ the dependence of u_p on ζ is almost fully lost for relatively high ζ potentials.

If the polyion is *fully drained*, a situation which is most readily approximated in systems with high ionic strength, the electrical mobility of the polyion may be expected to approach the mobility of a (charge carrying) *segment*. Points in favour of this 'monomer theory' are observations that λ_p generally does not depend very much on the molecular mass of the polyion and that it may have values in the same order of magnitude as small ions. The overall friction coefficient of the polyion would *then* simply be $f_{segment}$, referring to an elementary charged unit of the polyion. The total electrical force zeE (z being equal to the number of monovalent charged groups (segments), e the unit charge and E the applied field) is exerted on the complete polyionic entity with charge ze. However, the resulting 'monomer theory' is for many cases too rough. It ignores association of counterions, thus overestimating the charge of the monomer, and hydrodynamic interactions between different monomers, leading to overestimation of the mobility.

It is much more rewarding to consider the freely drained polyelectrolyte coil as a charged cylinder (see Fig. 2). A qualitative, lucid outline of the electrophoresis of random coil cylindrical polyions has been given by *Overbeek and Wiersema* [12]. Basically, the polyion is modelled as a thin sphere in which the liquid has the same viscosity as bulk liquid. As with the undrained sphere, part of the structural polyionic charge ze is compensated by counterions within the sphere and the remaining part (usually denoted by $z_{eff}e$) by counterions outside the sphere. Taking into account the hydrodynamic frictions inside and outside the sphere, but ignoring the relaxation effects, the resulting expression for the electrophoretic mobility is given by:

$$\frac{u_p}{e} = \frac{n(z - z_{eff})}{z f_{segment}} + \frac{z_{eff}}{G(\chi)} - \frac{z_{eff} \kappa_D a_s}{6 \pi \eta a_s (1 + \kappa_D a_s)} \tag{12}$$

where $G(\chi)$ is defined by:

$$G(\chi) = \frac{9(\chi - \tanh \chi) z f_{segment}}{2n[\chi^3 + \tfrac{3}{2}(\chi - \tanh \chi)]} \tag{13}$$

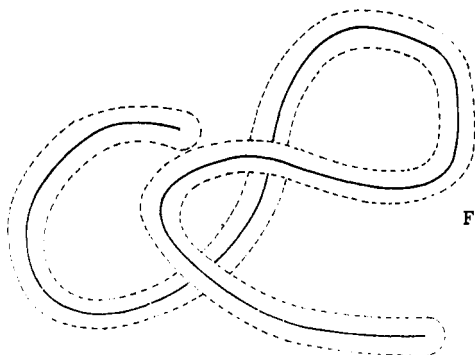$$\chi^2 = \frac{3 z f_{segment}}{4 n \pi \eta a_s} \tag{14}$$

Fig. 2. Schematic representation of a coiled polyion together with its double layer (interrupted curve) under conditions where cylindrical symmetry is operational.

The first term on the right hand side in eq. (12) represents the effects of the countercharge *inside* the coil (z-z_{eff}) and the corresponding charged segments. The second term may be conceived as the main hydrodynamic term of the coil with effective charge z_{eff} and the third term corrects for the retardation due to the counterions *outside* the sphere. The parameter χ is related to the degree of drainage of the coil. For *large* χ (little drainage) the function $G(\chi)$ approaches $6\pi\eta a_s$ and the coil will behave as a compact impermeable sphere (see above). On the other hand, for *low* χ drainage will be almost complete and:

$$\frac{u_p}{e} = \frac{n}{f_{segment}} \tag{15}$$

i.e., the limit of the 'monomer theory'. This limit is not very realistic since with the corresponding highly expanded coil, screening effects will be strong (see also the discussion above).

The line charge model. The basic electrostatic feature of a chain-like polyion is its spatially linear arrangement of charged groups. Under usual conditions of ionic strength and molecular mass, electrostatic interaction between different groups of the same polyion occurs over distances *small* as compared to the average end-to-end distance of the macromolecular entity. Furthermore, for not too weakly charged polyions and not too high ionic strengths the spacing ℓ between the charged sites is not much larger than the *Debye* screening length κ_D^{-1} so that electrostatic interaction between sites is important. Hence it is reasonable to model the polyion as an infinite line with a smeared-out charge. As the elementary parameter we shall use the dimensionless line charge density ξ, defined by:

$$\xi = \frac{\ell_B}{\ell} \tag{16}$$

where ℓ_B is the *Bjerrum* length, for monovalent groups given by:

$$\ell_B = \frac{e^2}{4\pi\epsilon\epsilon_o kT} \tag{17}$$

On the basis of purely electrostatic arguments it has been deduced [4] that in dilute pure polyelectrolyte solutions (no co-ions) ξ cannot exceed $|z_c|^{-1}$. This comprises the basic result of what has become known as the counterion condensation theory. If the value of ξ is higher than $|z_c|^{-1}$ a number of counterions is electrostatically forced to stay in the immediate vicinity ('condensed') of the polyion, so as to reduce the effective charge to the upper limit $|z_c|^{-1}$. The remaining counterions are not completely free, but constitute the more traditional *Debye-Hückel*-like countercharge atmosphere of the polyionic species.
        Starting from the *Nernst-Planck* equation for the migration of the small ions, taking into account the locally inhomogeneous electric field generated by the polyions, *Manning* [4] derived that for the distribution coefficient f of the counterions in a salt-free polyelectrolyte system:

$$f = 0.866|z_c|^{-1}\xi^{-1} \qquad (\xi \geq |z_c|^{-1}) \tag{18}$$

The dimensionless coefficient 0.866 originates from the evaluation of a numerical series (resulting from the *Fourier* components of the inhomogeneous polyion field). For $|z_c|\xi < 1$ the functionality is a different one, but normalized in such a way that agreement is

achieved for the break-point $|z_c|\xi = 1$. For the salt-free case and *monovalent* counterions, the expression for the low charge density regime ($\xi \leq 1$) has been given as [13]:

$$f = 1 - \frac{0.55\xi^2}{\pi + \xi} \qquad (\xi \leq 1) \qquad (19)$$

The expressions eqs. (18,19) for f may be combined with eq. (2) to serve as the analytical working equations. On the other hand, these expressions for f can be used to calculate the relaxation effect in the conductance of polyelectrolytic systems [13]. Starting-point is *Henry's* expression [10] for the electrical mobility of randomly oriented, infinitely long cylinders:

$$u_p' \approx \frac{2\epsilon\epsilon_0\zeta}{3\eta} \qquad (20)$$

where the prime in u_p' indicates that only the electrophoretic effects are taken into account (to distinguish it from u_p, in which the relaxation effect is included as well). Equation (20) is valid under the condition that the radius a of the cylinder is small compared to the *Debye* screening length ($\kappa_D a \ll 1$), a condition that certainly holds for dilute, (essentially) salt-free systems. The real mobility u_p can be found from eq. (20) after correcting for the relaxation field effect. According to *Manning's* concept, this effect can be formally identified with the retardation of the *uncondensed* counterions. Considering that for $|z_c|\xi > 1$ a fraction 0.866 of the counterions move 'freely' in the applied field E, and a fraction (1-0.866) travels in the opposite direction with the mobility of the polyion, it can be deduced from eq. (18) that:

$$\frac{E_{eff}}{E} = 0.866 - 0.134 \frac{u_p}{u_c^0} \qquad (21)$$

where E_{eff} is the effective field which is *lower* than the applied field due to the electrostatic polyion-counterion interactions. In eq. (21), migration of counterions along the polyion chain is ignored. It is useful to note here that $\frac{E_{eff}}{E}$ is identical to *Overbeek's* $(1-\frac{\Delta E}{E})$ [5]. Thus, with:

$$\frac{u_p'}{E} = \frac{u_p}{E_{eff}} \qquad (22)$$

it follows from eq. (21):

$$u_p = \frac{0.866 u_p'}{(1 + 0.134 \frac{u_p'}{u_c^0})} \qquad (23)$$

Before combining this result with eq. (20), we replace the ζ-potential by its limiting form for dilute solutions ($\kappa_D a \ll 1$) [4]:

$$|\zeta| \approx 2\xi_{net}\frac{RT}{F} |\ln \kappa_D' a| \qquad (24)$$

where, for the considered case of $|z_c|\xi > 1$, $\xi_{net} = |z_c|^{-1}$, and where κ_D' is a newly defined reciprocal screening length. For monovalent groups:

$$(\kappa_D')^2 = \frac{F^2}{\epsilon\epsilon_0 RT} \xi^{-1} c_p \qquad (\xi \geq 1) \qquad (25)$$

It is noted that the formulation in eq. (25) of the screening constant implies that the original term $\sum_{i,j} c_{i,j} z_{i,j}^2$ in eq. (10) is replaced by the equivalent concentration $\xi^{-1} c_p$ of the uncondensed monovalent ions. This corresponds to counting only those counterions that are responsible for the screening of the net charge ξ_{net}. Substitution of eqs. (25) and (20) into (23) finally yields for the electric conductivity ($F u_p$) of a polyion with monovalent groups:

$$\lambda_p = \frac{0.866 H \lambda_c^0 |\ln \kappa_D' a|}{|z_c|\lambda_c^0 + (1-0.866)H|\ln \kappa_D' a|} \qquad (26)$$

where H is a standard electrophoretic mobility factor defined by (compare eq. (6) or (20)):

$$H = \frac{4\epsilon\epsilon_0}{3\eta} RT \qquad (27)$$

It is perhaps rewarding to add that eq. (26) is most frequently quoted in its original form, that is, in terms of an outdated unit system and with combinations of numerical coefficients that fully destroy its transparency. We would like to promote the use of formulations such as given in eq. (26). With the derivation of eq. (26) for λ_p, together with eq. (18) for f, we can return to the starting equation, eq. (2), for the conductivity of the complete polyelectrolytic system.

A somewhat more elaborate derivation of λ_p - holding for a linear array of discrete point charges instead of the (rather implicit) previous smeared-out line charge - has also been proposed [14]. The results of this theory are largely similar to the equations above but allow the inspection of the influence from (a single) added salt. We finally remark that one of the main assumptions results in the phenomenological approach, i.e., λ_p being independent of the nature of the counterion, is largely in line with eq. (26). The term $0.134H|\ln \kappa_D'a|$ in the denominator is of second order and usually less than 10 % of the term $|z_c|\lambda_c^{\circ}$ (compare eq. (23)). Thus the relationship between Λ and λ_c° will indeed be found to be practically linear.

III. EVALUATION OF EXPERIMENTAL DATA AND APPLICATIONS

Conductometry is increasingly applied to study properties of polyelectrolyte solutions and complexation reactions of polyelectrolyte systems. From experimental studies, a number of characteristics of the conductivity of polyelectrolyte solutions are well established [1,15]. For instance, there exists sufficient evidence, although still disputed [16] for the insensitivity of the polyion conductivity to the degree of polymerisation of the polyelectrolyte. Still, the interpretation of a number of experimental findings remains difficult. Suggested interpretations do not always cope with the newer theoretical framework, and sometimes lead to conflicting opinions.

Most often, experiments are performed using conventional types of conductometers, with platinum or platinized electrodes and with cell constants in the order of magnitude of $0.1 - 10$ cm^{-1}. Accuracies in the conductivity reading are generally in the range $99.5 - 99.9$ %. Frequencies applied are about 2-4 kHz. It has been reported that for sulphostyrene based and acrylic polyacids, λ_p is not dependent on the applied frequency over the commonly applied range [7,17,18]. No experimental evidence was found for effects on λ_p at higher frequencies.

In this section, recent experimental work on conductometry of polyelectrolyte solutions will be critically reviewed. Classical work has been reviewed by *Kurucsev* and *Steel* [1]. On the basis of their direction, subjects of experimental studies can be classified into three main categories:
(i)   association phenomena (including the properties of λ_p);
(ii) quantitative analyses of charged groups;
(iii) conformational changes.

III.1 Association phenomena

Counterion association
In polyelectrolyte solutions, the polyions as well as the counterions contribute to the conductivity of the solutions. The conductivity of a solution of pure polyelectrolyte (i.e., with no other ions than the polyion and its counterions) is much lower than that of the corresponding non-polymeric salt solution. This is primarily the result of the association of counterions that reduces the effective mobility of the counterions. With changing extent of counterion binding, for instance as a result of further charging of the polyion, the value of λ_p may change as well [8,19].

Counterion association has been extensively studied by widely different methods [15,20]. It has been stressed by *Mandel* [21] that different methods may be sensitive to different aspects of the counterion/polyion association. Conductometry responds to the net effect of *all* ionic species in solution, and is *a priori* a valuable method to study processes in which the mobilities of certain ions are affected.
Conductometric studies of counterion association with polyelectrolytes and the corresponding behaviour of λ_p are mainly focussed on:
(i)   the behaviour of the *distribution parameter* f_i and the *polyionic conductivity* λ_p in simple and mixed systems;
(ii) the *characterization of specific complexation* between metal ion and polyion (involving intrinsic chemical interaction);
(iii) the polyelectrolyte *concentration dependence* of the counterion association and λ_p.

Distribution parameter and polyionic conductivity. The charge parameter ξ controls the counterion binding. Its structural value ξ_{str} is the maximum of ξ as defined by the density of the chargeable groups on the polyion. For systems with sufficiently high ξ, condensation of counterions results in a decrease of the value of ξ to a net value ξ_{net}. Studies of the

TABLE 1. Line charge densities ξ, and corresponding experimental values of the distribution parameter for monovalent counterions f_+, for a number of polyelectrolytes in aqueous solution at ~20 °C.

Polyelectrolyte		ξ	f_+	Ref.
Na poly(styrenesulphonate)		3.14	0.32	[9]
Na polyphosphate		2.85	0.30	[22]
poly(vinylpyridinium bromide)		2.85	0.30	[23]
poly(vinylbenzyltrime-thylammonium chloride)		2.85	0.28	[23]
Na polyacrylate		2.80	0.38	[2]
Na polyacrylate		2.56	0.35	[24]
Na polyacrylate		2.32	0.38	[2]
Na polyacrylate		1.77	0.45	[2]
Na polygalacturonate		1.63	0.53	[25]
Pectin	DE*)< 2 %	1.58	0.62	[26]
Na alginate		1.43	0.61	[25]
DNA (denaturated)		1.05	0.67	[27]
Pectin	DE*)= 38.1 %	1.00	0.78	[26]
Pectin	DE*)= 58.2 %	0.67	0.86	[26]
Pectin	DE*)= 83.0 %	0.27	0.94	[26]

*) DE: degree of esterification

relation between ξ and f_i (or θ_i) have been carried out to reveal the existence of a critical value ξ_{crit} (depending on the valence of counterion) beyond which condensation is supposed to occur. Experimentally, changes in ξ are introduced either by chemically changing the number of charged groups (e.g., by partial esterification or neutralization in the case of weak polyacids and polybases), or by metal ion titration into the polyelectrolyte system.

As stressed before, the finding that Λ and λ_c^o show a linear relation [5,8,9] enabled the determination of f and λ_p. Experimental values of f_+ for different polyanionic systems are collected in Table 1. In Fig. 3 the values of Table 1 are depicted and compared with the theoretical curve of f versus ξ for monovalent counterions in salt-free systems as predicted by the *counterion condensation* theory. Additionally the f/ξ-curve for divalent counterions is pictured. It can be concluded that the trend in the data is well covered by the theory.

As an outcome of the condensation theory, an explicit expression has been given for λ_p, amenable to experimental verification. According to eq. (26), λ_p is essentially dependent on the type of counterion involved. Experimental evidence of this dependency has been reported for polystyrenesulphonates [28], but was not found for polymethacrylate salts [8]. Experimental values of λ_p of acrylic polyacids in salt-free solutions are in the range from 40 to 60 $S.mol^{-1}.cm^2$ [19,29,30].
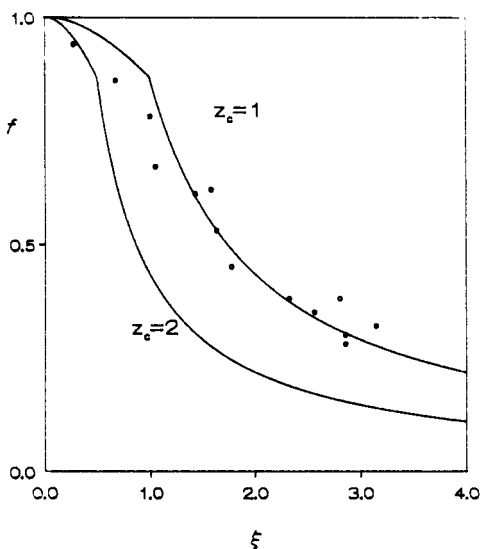

Fig. 3. The distribution parameter f versus ξ in salt-free systems. Curves: condensation theory. Points: experimental data (Table 1).

There is no agreement on the dependency of λ_p on α_n (which is linearly related to ξ). A small change of λ_p with α_n has been reported [8,18] for poly(methacrylic acid) andpoly(acrylic acid), whereas old data report an increase for poly(acrylic acid) [31] and a decrease for poly(methacrylic acid), from about 40 to 13 over the range $0.1 < \alpha_n < 0.8$ [19]. It is noted that due to the dependence of ℓ_D' on ξ (in eq. (25)) the condensation theory predicts a slight increase of λ_p with α_n for systems without added salt. Such a dependence was indeed found for pectins at different values of ξ: λ_p increasing from 45 to 60 $S.mol^{-1}.cm^2$ from ξ increasing for 1.0 to 1.6 [26]. For humic acids, mainly bearing carboxylic groups, λ_p values have been found to be in the range 45 to 55 $S.mol^{-1}.cm^2$ [29]. It is remarkable that most λ_p values reported for different types of polycarboxylic acids are rather close, about 50 $S.mol^{-1}.cm^2$, not too far from the value of λ for monomeric entities such as the acetate ion: 41 $S.mol^{-1}.cm^2$. For H-CMC it was reported that [32] $\lambda_p = 48$ $S.mol^{-1}.cm^2$ ($c_p = 5$ $mmol.l^{-1}$).

An important feature of the condensation theory is the valence dependency of ξ_{crit}. In the case where both monovalent and divalent counterions are present in a polyelectrolyte solution, the value of ξ_{net} may be expected to be neither 1 nor $\frac{1}{2}$. Only at high ξ (corresponding with high α_n), the exchange ratio Me^{2+}/Me^+ in the case of acrylic polyacids was found to be close to unity, and distinctly higher in the low ξ range [9]. On one hand this shows that even at low Me^{2+}/Me^+ ratios simple charge balance considerations do not apply and on the other hand it suggests that more or less discrete changes in the ion binding characteristics occur.

Bratko et al. [33] found experimental evidence for the numerical solution of the *Poisson-Boltzmann* equation to calculate f_+ and f_{2+} in the case of sulphostyrene-based polyacids, partly neutralized with Mg^{2+}.

Characterization of specific complexation. *Since f represents the fraction of counterions that are not influenced by binding or charge effects of polyelectrolyte, this parameter is expected to be related to the counterion activity coefficient* γ_i. *According to Manning* [34] f_i *is linearly related to* γ_i. *Thus, conductometrically determined values of f can be used to calculate stability constants.*

Usually data from conductometric titration are represented as the *difference* between the specific conductance of the *mixture* of polyelectrolyte + titrant, and the *sum* of the *separate* polyion solution and metal salt solution [9,35,36,37] yielding a *conductivity excess* function $\Delta\kappa$. In Fig. 4, a typical result of a conductometric metal ion titration is presented. Positive values of the $\Delta\kappa$ function demonstrate association of the Me^{2+} ions with the polymethacrylate ion. The value of the slope of the $\Delta\kappa$-function indicates the degree of association of the divalent metal ion. At high values of ξ, for sufficiently large α_n, the $\Delta\kappa$-function remains small at the onset of the titration, due to the exchange process qNa^+/Zn^{2+}, with $0 \le q \le 2$ [37]. The different changes in the slope of the $\Delta\kappa$-function are the result of the electrostatic features of the mixed system. To attribute those changes to different coordination numbers of the ZnPMA complexes [36], is therefore premature.
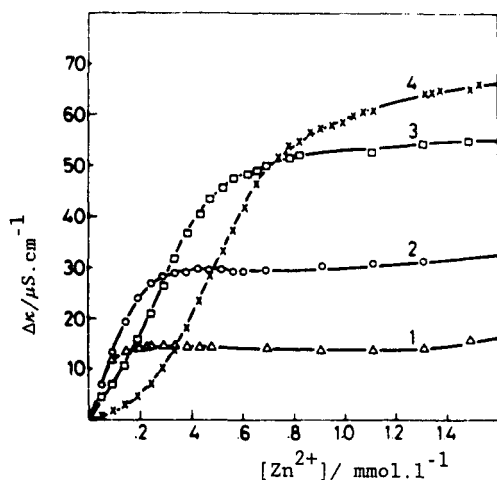

Fig. 4. The conductivity excess function $\Delta\kappa$ versus the concentration $Zn(NO_3)_2$ in a titration of PMA. [PMA] $= 2.50$ $mmol.l^{-1}$. $\alpha_n = 0.15$ (1), 0.25 (2), 0.50 (3), 0.70 (4).

Whether the ion binding is purely electrostatic or contains ion-specific chemical contributions, cannot be derived from conductometric experiments. Only in those cases where due to a substitution reaction of the type:

$$H\text{-polyion} + Me^+ \rightarrow Me\text{-polyion} + H^+ \qquad (28)$$

where the proton is to some extent *specifically* bound, a measurable contribution is made by the substituted ions, with the net result in $\Delta\kappa$ indicating ion-specificity. For the binding of heavy metal ions to acrylic polyacids, there is conductometric evidence that the ion-specific character *decreases* in the order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ba^{2+}$ [37]. The binding of Ca^{2+}, Sr^{2+} and Ba^{2+} to CMC appeared to be purely electrostatic, and the fraction 'free' Me^{2+} was reported to be equal to the activities of Me^{2+} in the MeCMC systems [38]. For CMC, the degree of association was reported to decrease in the sequence: $Li^+ > (C_4H_9)_4N^+ > Na^+ > (CH_3)_4N^+$ [32].

As the $\Delta\kappa$-function is related to the fraction bound metal ions, binding constants for the formation of the metal-polyelectrolyte complex can, under favourable conditions, be determined from conductivity measurements. However, additional information must be available for instance with respect to the complex stoichiometry, the magnitude of λ_p, the degree of ion-specificity of the binding involved, and the characteristics of the polyacid or polybase involved.
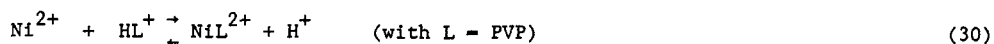
Binding constants of metal/nuclease interactions were determined by conductometric titrations at low protein concentrations ($10^{-6} - 10^{-5}$ mol.l^{-1}) [39]. With some simplifying assumptions, the *conductivity excess* function $\Delta\kappa$ was considered to be proportional to the bound fraction in these systems. Thus, the change of $\Delta\kappa$ in the course of the titrations enabled the construction of *Scatchard* plots, from which the binding parameters were deduced. Intrinsic binding constants K_{int} for the complexes Cu-RNase A, and Cu-RNase B, appeared to be 7.3×10^5 mol^{-1}.l and 6.5×10^5 mol^{-1}.l, respectively, whereas the values of K_{int} for Mn-DNase I and for the interactions of cytidine-3'-monophosphate with RNase A and RNase B were all in the order of magnitude of 1.2×10^5 mol^{-1}.l [39].

Values of K_{int} for the binding of heavy metals to acrylic polyacids were estimated from conductometric titrations using the additional information that a substantial increase in the release of H^+, according to eq. (28), becomes manifest at that point in the conductometric titration with Me^{2+}-ions where ξ_{net} has become very low. With some approximations, it was deduced that, if $d[H^+]/d[Me^{2+}]_{added}$ is at a maximum value [37]:

$$K_{int} \approx \frac{d[H^+]}{d[Me^{2+}]} \times \frac{2[H^+]K_{a,int}^{-1}}{(1 - \alpha_d)c_T} \qquad (29)$$

where α_d is the degree of dissociation, $K_{a,int}$ the intrinsic dissociation constant of the acrylic polyacid, and c_T the total concentration of functional groups. The thus estimated values of K_{int} for the systems Pb,Cd,Zn/PMA at $\alpha_n = 0.40$ were 1.1×10^2, 2.1 and 0.7 mol^{-1}.l respectively, whereas those for the systems Pb,Cd,Zn/PAA at $\alpha_n = 0.40$ appeared to be $> 3 \times 10^4$, 9.2×10^2 and 1.3×10^1 mol^{-1}.l, respectively. The values agreed with the more accurate values determined by polarography [37].

The kinetics of complex formation have also been studied conductometrically. The complexation of poly(4-vinylpyridine) (PVP) with Ni^{2+} was investigated by *Okubo* and *Enokida* [40] using the stopped-flow technique, which allows the measurement of changes in conductometry in the 0.01 - 1 s range. As PVP is a weakly alkaline polymer, the charging (with H^+) is enhanced with decreasing pH. The increase in relaxation time τ with decreasing pH was explained by strong electrostatic repulsion between the Ni- and PVP-cations. With addition of simple salt to the Ni^{2+}-PVP methanol/water system, τ initially decreases as a result of screening effects, and increases at higher concentrations of simple salt, probably as a result of coiling of the polymer. The forward reaction rate constant k_f for:

$$Ni^{2+} + HL^+ \underset{\leftarrow}{\overset{\rightarrow}{\rightleftharpoons}} NiL^{2+} + H^+ \qquad \text{(with } L = PVP) \qquad (30)$$

was found to be smaller than those for Ni^{2+}-imidazole systems. This is explained by the electrostatic repulsive interactions between Ni^{2+} and the partially protonated polyions.

<u>Concentration dependence</u>. The concentration dependence of a number of physico-chemical properties of polyelectrolytes, for instance the viscosity, the counterion binding and the ionic conductivity, shows anomalous behaviour. According to the condensation theory, λ_p
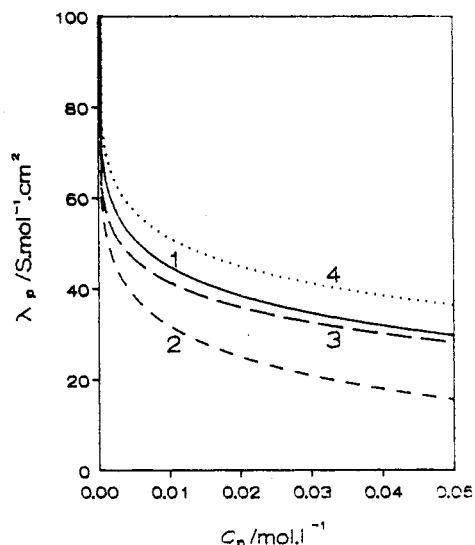
Fig. 5. Theoretical dependence of λ_p on c_p.

1. $\xi=2.85$, $a=0.8$ nm, $\lambda_c^{\circ}=73.5$ S.mol^{-1}.cm^2;

2. $\xi=2.85$, $a=1.6$ nm, $\lambda_c^{\circ}=73.5$ S.mol^{-1}.cm^2;

3. $\xi=2.85$, $a=0.8$ nm, $\lambda_c^{\circ}=38.7$ S.mol^{-1}.cm^2;

4. $\xi=5.70$, $a=0.8$ nm, $\lambda_c^{\circ}=73.5$ S.mol^{-1}.cm^2;

decreases with increasing concentration as a result of the increase of $|\ln \kappa_D'a|$. In Fig. 5 the theoretical dependence of λ_p on c_p calculated according to eq. (26), for -20°C, is pictured for several values of a, ξ and the values of λ_c° for K$^+$ and Li$^+$. It is noted that for acrylic polyelectrolytes $\xi_{str} = 2.85$ and $a = 0.8$ nm. Figure 5 visualises that theoretically in salt-free systems λ_p decreases with increasing polyion radius a, decreasing counterionic conductivity λ_c° and decreasing line charge density ξ.

In most cases a decrease of Λ with increasing concentration was reported [17]: e.g., for polyacrylates and polymethacrylates [7,41], poly(ethylenesulphonate)s [42], sodium carboxymethylcellulose [43], dextran sulphates (DS) [44] and κ-carrageenan [45]. In some cases a minimum in Λ is observed, e.g., for poly(ethylenesulphonic acid) [42] and sodium polystyrenesulphonate [46]. For sulphostyrene based polyelectrolytes the polyionic conductivity was found to increase with decreasing polyion concentration, and to pass through a maximum at very low concentrations [47]. However, both Jordan et al. [48] and Vink [30] reported Λ to be practically concentration independent for sodium polystyrenesulphonate. This behaviour was explained in terms of specific hydrogen ion-polyion interactions. According to Vink [30] the steep decrease in Λ at low c_p, for different KCMC salts, is parallelled by a steep decrease in f, and only a slight decrease in λ_p, indicating that the counterion binding is not independent of the polyelectrolyte concentration.

Joshi and Kwak [44], referring to various authors, report that the disentangling of the concentration dependencies of f and λ_p results in different conclusions for different polyelectrolytes: for instance for NaPAA f was found to be concentration independent whereas for MeDS (Me = Li, Na, K) f appeared to increase with increasing polyion concentration. Moreover the order Li$^+$ > Na$^+$ > K$^+$ for the f values of MeDS was not obeyed for the values of λ_p. In spite of numerous data, the concentration dependence of the conductivity of polyelectrolyte solutions is still not fully understood. The influence of counterions on the local viscosity around the polyion, the conformation, and the ion-specificity of the binding complicate the elucidation of that dependence. Kwak et al. [49] concluded for a number carboxymethylcelluloses and pectates that the concentration dependence predicted by the condensation theory is in agreement with the observations only at relatively low charge densities. The same conclusion was reached by Miyamoto [50] for a copolymer of iso-butyl vinyl ether and maleic acid. This seems to be a sound rationale, since the approximations involved in the derivation of eq. (26) include a low-amplitude relation between ξ and the ζ-potential (eq. (24)). It is noted that for polysoaps (with long side-chains: large a), Λ is smaller than for the corresponding polyelectrolytes [51].

Experiments at low concentrations revealed that for mixed systems (simple salt + polyion) the resulting conductivity does not obey an additivity rule [52].

Polyion/polyion association

Mutual interactions between weakly acidic (or basic) and strongly basic (or acidic) polyions have been studied conductometrically by the stopped-flow technique by Okubo et al. [53], to elucidate the dynamic parameters involved. For both the reaction of polyethyleneimine (PEI) with poly(ethylene sulphonate) (PES), and sodium polyacrylate (NaPAA) with 'polybrene' (PB) (see Note), two relaxations were observed on rapid mixing of the reactants: a rapid increase (time constant τ_1) and a decrease (time constant τ_2) in

conductance. The r_1-process was attributed to the association reaction whereas the r_2-relaxation was considered as a result of a reorientation of the complex conformation of the polyion. Using r_1, the reaction rate constants of the formation of the polyion complexes k_f could be determined. The values of k_f, ranging from $\approx 10^6$ - 10^7 $mol^{-1}.l.s^{-1}$, increased with increasing charge density of the weakly acidic (or basic) reactants, and decreased with increasing concentration 1:1 salt. Both trends are readily understood from electrostatic arguments.

   The complexation of poly(acrylic acid) (H-PAA) with polyvinylpyrrolidone (PVPI), was studied conductometrically and by the stopped-flow technique [54]. As the reaction between H-PAA and PVPI inhibits further dissociation of H-PAA, the measured values of stability constants can be exploited to calculate the degree of complexation. For 15 °C it was found that the stability constant $K_{stab} = 2.3x10^3$ $mol^{-1}.l$ and reaction rate constant $k_f = 1.3x10^5$ $mol^{-1}.l.s^{-1}$.

   The stoichiometry of complexation in the system polystyrene latex/polylysine.HBr-L was studied conductometrically by *Bonekamp* and *Lyklema* [55], reporting a 1:2 ratio whereas for poly(styrenesulphonic acid)/polylysine.HBr-L a 1:1 ratio was found.

III.2 Quantitative analyses of charged groups

Conductometric acid/base titrations can be applied to determine the total number of chargeable groups of polyacids or polybases. The titration curves yield end-points that under certain conditions are better defined than those in the corresponding potentiometric curves. Conductometric acid/base titrations have been reported for humic acid (HA) [29,37,56,57,58,59,60,61,62], polyvinyl ether/maleic anhydride copolymers [51], fulvic acids (FA) [63], kaolinitic clays and clay-humic acid complexes [64], carboxymethyl-cellulose (H-CMC) [32,38], poly(acrylic acid) (H-PAA), poly(methacrylic acid) (H-PMA) [37], chondroitin sulfuric acid, heparin [65], polystyrene latices [55,66], and pectins [26].

   A typical form of the conductometric curve for the titration of a weak polyacid is given in Fig. 6, which also shows the corresponding potentiometric titration curve. The change of the conductivity $\Delta\kappa$ is plotted as a function of the degree of neutralisation α_n. For $0 \leq \alpha_n \leq 1$ the curve consists of a descending and a rising part. A simple description of the curve has been given by *Rinaudo* and *Daune* [67]. The initial part of the curve, up to the local minimum, predominantly represents the neutralization of (autodissociated) H^+ by added KOH, corresponding with:

$$H^+ + L^- + K^+ + OH^- \rightarrow H_2O + L^- + K^+ \tag{31}$$

For $\alpha < \alpha_{n(min)}$, and $[OH^-]$ sufficiently low, $\Delta\kappa$ is approximately given by:

$$\Delta\kappa = \lambda_H[H^+] + \lambda_p[L^-] + \lambda_K[K^+] - \kappa_{(\alpha_n=0)} \tag{32}$$

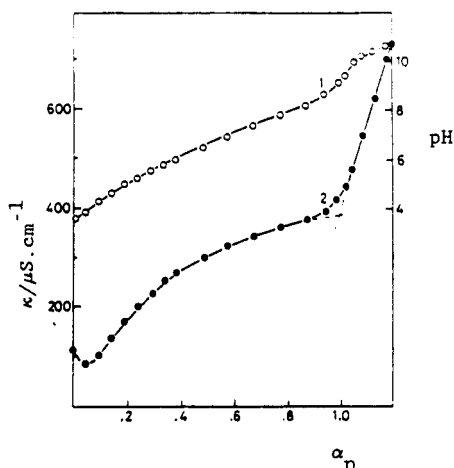where the concentrations refer to those ('free') species that contribute to the

Fig. 6. Titration of PAA with KOH. [PAA]=10.4 mmol.l^{-1}. M=300,000. No added salt. 1. pH; 2. conductivity.
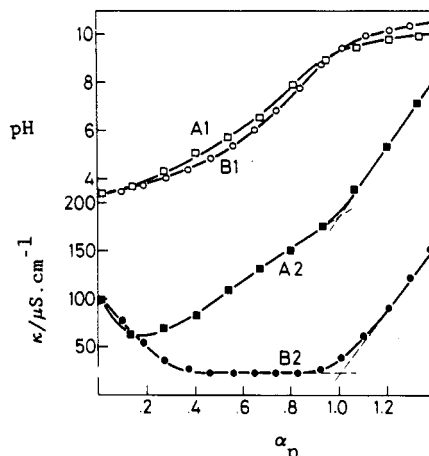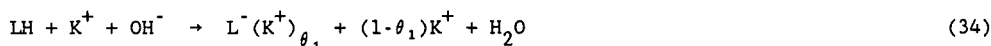
Fig. 7. Acid/base titration of HA (Fluka). [HA]=1.85 mmol.l^{-1}. No added salt. A. KOH; B. Ba(OH)$_2$; 1. pH; 2. conductivity [37].

Note: Polybrene = 1,5-dimethyl-1,5-diaza-undeca-methylene polymethobromide, hexadimethrine bromide

conductivity, and $\kappa_{(\alpha_n=0)}$ is the initial conductivity of the solution at the onset of the titration. The decrease in κ is due to the decrease in $[H^+]$, since both $[L^-]$ and $[K^+]$ increase as the titration proceeds. The concentrations in eq. (32) can be expressed in terms of α_n and the *apparent* dissociation constant of the polyacid, K_a. Then, for the minimum in the curve, were $d\kappa/d\alpha_n = 0$, it follows that:

$$\alpha_{n(min)}^2 = \frac{\lambda_H K_a}{(\lambda_p + \lambda_K)c_T} \qquad (33)$$

Thus, the position of the minimum gives an impression of the acid strength at low α_n. For systems of weak polyacids with small amounts of added salt, the minimum shifts to higher values of α_n [37], due to the screening effect, which enlarges the value of K_a. Ultimately, a large amount of added 1:1 salt would result in an approximately linear decrease of κ with α_n, as found for strong (poly)acids, such as polystyrenesulphonate [68]. In the case of specific binding of cations of the added salt, the shift in the minimum is much more pronounced, even at low salt concentrations.

For $\alpha_n \gg \alpha_{n(min)}$, where the analytical concentrations of L^- and K^+ linearly increase with α_n and where the H^+-ions no longer (and the OH^--ions not yet) measurably contribute to $\Delta\kappa$, the increase in $\Delta\kappa$ levels off with increasing α_n. The straightforward interpretation is that binding (condensation) of K^+-ions occurs at elevated values of α_n, where $\xi > 1$, and the neutralisation reaction for weak polyacids can now be represented as:

$$LH + K^+ + OH^- \rightarrow L^-(K^+)_{\theta_1} + (1-\theta_1)K^+ + H_2O \qquad (34)$$

where θ_1 is equal to the number of K^+ bound per L^-. For $[K^+] = (1-\theta_1)\alpha_n c_T$ and $[L^-] = [K^+]$, $\Delta\kappa$ can be expressed as:

$$\Delta\kappa = (1-\theta_1)\alpha_n c_T(\lambda_p + \lambda_K') - \kappa_{(\alpha_n=0)} \qquad (35)$$

where λ_K' is the ionic conductivity of the 'free' K^+-ions (not condensed).

Figure 6 shows that for $\alpha_n \gg \alpha_{n(min)}$, θ_1 (in eq. (35)) increases with α_n. This increase in θ_1 determines the sharpness of the end-point of the titration. The potentiometric titration curve (see also Fig. 6) merely reflects the gradual increase of the apparent K_a-value which smoothes the curve rather than sharpens it at the end-point of the titration.

Conductometric titrations have been frequently applied in the case of humic acids (HA) and fulvic acids (FA). HA and FA are *mixtures* of naturally occurring polymeric acids with a wide distribution of K_a-values [69]. For this humic material *polyelectrolytic* effects as well as *mixture* effects determine the gradually changing value of the apparent K_a at different degrees of neutralization. In Fig. 7, potentiometric and conductometric titration curves are given for HA (Fluka sample) using KOH and Ba(OH)$_2$, respectively, as titrant. The smoothness of the pH-curve, as a result of the above-mentioned effects, does not allow a reliable end-point determination, whereas in both the conductometric curves an end-point is well defined. The curve of the HA titration with an alkaline metal hydroxide differs markedly from that with an alkaline earth metal hydroxide (see Fig. 7) [29,37,58,61], indicating that the degree of association of divalent counterions is higher than that of the monovalent ones. The same result was obtained for the titration of H-CMC with Ba(OH)$_2$, Ca(OH)$_2$ and Sr(OH)$_2$ [38].

The discernible parts of the conductometric titration curve of HA, clay-HA and FA have also been interpreted as reflecting different types of functional groups [70]. *Gamble* [63] attributed the descending part of the curve to strongly acidic carboxylic groups (on aromatic rings, ortho to phenolic-OH groups) and the rising part to more weakly acidic carboxylic groups. *Arai* and *Kumada* [29,60] categorized very weak (VW), weak (W) and strong (S) acidic functional groups, based on distinguishable stages in the titration curve. *Lockhart* [71] distinguished COOH and phenolic-OH groups on HA, and -MeOH$_2^+$, -MeOH and -MeO$^-$ groups (Me = Al,Fe) on the clay surface. *Schnitzer* and *Skinner* [72] proposed not less than four different functional groups on HA as an outcome of the conductometric titration curve. Although *polyelectrolyte* and chemical *heterogeneity* ('mixture') effects are difficult to separate, the conductometric titration curve for humic material can be satisfactorily explained supposing *one* type of group only and purely electrostatic association [37]. An alternative way to distinguish different groups is the titration with different titrants. *Gaberman* and *Litovko* [73] determined the carboxylic groups by titration with aqueous NH$_3$-solution. It was proven that phenolic hydroxyl groups (phenol, pyrocatechol and 1,2-dihydroxy-9,10-anthraquinone) do not react with NH$_3$. Also in the case of chondroitin

sulfuric acid and heparin, the 'breaks' in the curve of the conductometric titration, with sodium hydroxide as titrant, have been interpreted as the result of the presence of different functional groups on each of these polyelectrolytes [65]. However, the 'breaks' might just as well be explained by starting condensation of Na^+ ions. The least one can conclude from this is that interpretations in terms of a discrete number of functional groups are premature and probably incorrect. Discernible parts of conductometric titration curves should always be interpreted with care, taking into account the change of ξ in the course of the titration.

For poly(2-vinyl-pyridine) in aqueous solution without added salt, the degree of protonation appeared, in conductometric experiments, to be almost unaffected by the nature of the counterion (Cl^-, Br^-, NO_3^-) and by the stereoregularity of the polymer [74]. This finding provides additional evidence for the virtual independency of λ_p with respect to the λ_c, in the case of weak polybases.

III.3 Conformational changes of polyions

With increasing degree of charging of a rigid polyelectrolyte, the value of ξ increases and consequently the value of f (in eq. (1)) decreases during the charging process. The value of f as a function of ξ will show, according to the theory of *Manning* (see eqs. (18) and (19)), a discontinuity as ξ passes the value of $|z_c|^{-1}$. As a result of the increasing repulsion between the charged groups, non-rigid polyelectrolyte structures may gradually become more extended. Some polyelectrolytes will show a well-defined conformation transition. In these cases the decline of f with ξ will differ from that predicted for the rod-like model, and a comparison of the theoretical values (according the *condensation* theory) for the compact structure, often a helix, as well as the more extended structure, usually a random coil, with the experimental value, may elucidate the characteristics of the conformation change.

From an evaluation of f in the case of poly(acrylic acid), the rodlike model turns out to be inapplicable at low degrees of neutralization, whereas in the case of poly(D-glutamic acid) the helical structure at low α allows the applicability of the rodlike model in this region [22].

From conductometric experiments with a solution of xanthan, a polyanion with a pentasaccharide repeating structure, values of Λ have been determined as a function of the temperature over the range 20 °C to 60 °C. From comparison with the theoretical values of Λ using eqs. (1), (18) and (24) for different conformations, random-coil, single-helix and double-helix, over that temperature range, it appeared that at low temperatures the data were consistent with a single rather than a double helix [75]. In systems without added 1:1 salt, a transition helix → coil is observed at ~ 33 °C, with $\Delta b = 0.05$ nm, whereas in systems with added 1:1 salt, the order-disorder temperature appeared to be ≈ 62 °C with $\Delta b = 0.55$ nm.

The stopped-flow technique, has been applied by *Okubo* [54] to study conformation changes in poly(acrylic acid) (H-PAA) and polyethyleneimine (PEI). The relaxation times τ increased with increasing charging of H-PAA and PEI. Thus, τ-values for the rod-conformations were large whereas those for the coil-conformations were small.

Tuffile and *Ander* [25] concluded from carefully performed conductivity measurements that for sodium polygalacturonate the distance separating the charged groups is probably somewhat larger than the known crystallographic value of 0.437 nm. They concluded for both sodium polygalacturonate and its stereo-isomer sodium alginate that the rod-model is applicable in the description of their conductivity properties.

From the determination of f for the binding of Ca^{2+} to pectins, it was concluded by *Thibault* and *Rinaudo* [26] that the low values found, suggest an aggregation or dimerization of the pectins upon binding to Ca^{2+}, turning the solution to a gel.

From the results of conductometric titrations of PAA in *methanol* with CH_3ONa it was suggested that in the interval $0.10 < \alpha_n < 0.25$ a conformational transition occurs to a compact particle in which most of the carboxylate groups, carboxylic groups and also the counterions are supposed to be situated, whereas such transition was not observed in the titration with CH_3OLi [76].

Conductometric measurements with the stopped-flow technique allowed *Okubo* [77] to estimate the effective length of rodlike H-PAA molecules from the determination of the rotational relaxation time τ_r. The conformation appeared to be an expanded coil when the groups are not ionized. However, at high degrees of α_n, the effective length is close to the contour length, suggesting that the conformation is rod-like. The chain shrinks with decreasing α_n, and with increasing concentration. At $\alpha_n = -0.2$ (excess strong acid), the effective length for $M_{H-PAA} = 4x10^6$ is about 1 μm, whereas at $\alpha_n = 1$, the length is about 13.9 μm. It is noted by *Okubo* [77], that at $\alpha_n = 0$, the H-PAA molecules in deionized solutions are still rod-like, in accordance with the fact that the $(\kappa_D')^{-1}$- length is many times larger than the monomer length of 0.25 nm.

III.4 Concluding remarks

The examples presented in this chapter illustrate that conductometry provides a valuable tool in the study of polyelectrolytes in solution, in particular with respect to association phenomena and quantitative analysis of charged groups. Up to now, only the *counterion condensation* theory is a sufficiently elaborated polyelectrolyte theory which, on a qualitative level, explains the effects of association of counterions on the conductivity of systems containing polyions. The main advantage of conductometry is the possibility of a careful and sensitive book-keeping of the charges involved, that outweighs the non-selectivity of the method in its application in the field of polyelectrolyte research. Some concentration of simple salt is allowed, and any turbidity of the systems is not hampering the measurements. Conductometry is a *steady state* method that does not disturb the equilibrium studied.

A classical analytical method for the study of equilibria is potentiometry, which is a real *equilibrium* method as the measurement of the potential proceeds without current flow. Electrode potentials respond, often quite selectively, to the *activity* of the ion involved. However. the use of a relatively high concentration of supporting electrolyte is mandatory to ensure that the ion activities remain constant. Some electrodes, reversible to metal ions, behave erratically in the presence of polyelectrolytes, e.g., proteins, or attain equilibrium very slowly.

Polarography and voltammetry are *dynamic* methods, based on a current response. In their modern modes, i.e., in the pulse, square wave, phase sensitive a.c. and stripping modes, the sensitivity is substantially enhanced and detection limits down to 10^{-11} mol.1^{-1} may be reached. Measurements can be performed over a wide range of ionic strengths. As polyelectrolytes tend to adsorb at many types of electrodes, conditions have to be chosen under which the distortion of the signals is minimized. With metal/polyelectrolyte systems, complications arise from the differences between the diffusion coefficients of the metal/polyelectrolyte complexes and the electroactive metal ions. The theory becomes rather involved [78,79], especially if the metal/polyelectrolyte complex is not electrochemically labile.

Voltammetry (necessarily at rather high salt concentrations) can be used *complementarily* to conductometry (necessarily at low salt concentrations).

LIST OF SYMBOLS AND ABBREVIATIONS

a	cylinder radius of linear polyion
a_s	radius of spherical polyion
b	distance separating functional groups on the polyion
c	counterion
c	concentration
c_i, c_j	analytical concentration of counterions i, co-ions j
c_p	concentration of charged polyion groups
c_T	total concentration of (charged and uncharged) polyionic groups
D, $D°$	diffusion coefficient of metal ions in the presence, in the absence of polyions
e	unit charge
E, E_{eff}	electric field; effective electric field
f	distribution parameter of counterions (in eq. (1))
f_i, f_+, f_{2+}	distribution parameter of counterions i, of monovalent, divalent counterions
f_p	charge fraction of the polyion
$f_{segment}$	friction coefficient of polyion segment
F	constant of *Faraday*
$F(\kappa_D a_s)$	function in eq. (8)
$G(\gamma)$	term accounting for polyion drainage defined by eq. (13)
H	standard electrophoretic mobility factor defined by eq. (27)
k	constant of *Boltzmann*
k_f	forward reaction rate constant
K_a	*apparent* acid dissociation constant
$K_{a,int}$	intrinsic polyacid dissociation constant
K_{int}	intrinsic binding constant
K_{stab}	stability constant
ℓ	spacing between charged sites on polyion
ℓ_B	*Bjerrum* length
n	valency of a polyionic charged group

$p,\ p^{z-}$ polyion, negatively charged polyion with total charge z

q real number

R gas constant

T *Kelvin* temperature

$u_p,\ u_c^\circ$ electrical mobility of polyion, of counterion

u_p' expression for u_p in which the relaxation effect is not included

$z,\ z_{eff}$ polyion valence, effective number of polyion charges

$z_i,\ z_c$ charge of small ion i, counterion

$\alpha_d,\ \alpha_n$ degree of dissociation, degree of neutralization

$\alpha_{n(min)}$ degree of neutralization at the minimum of the titration curve

γ_i activity coefficient of species i

$\epsilon,\ \epsilon_\circ$ relative electrical permittivity, permittivity of free space

ζ elektrokinetic or zèta potential

η viscosity of the medium

$\theta_i,\ \theta_1,\ \theta_2$ fractional coverage by species i, monovalent ions, divalent ions

κ conductivity

$\Delta\kappa$ conductivity difference

κ_D *Debye* screening parameter, defined by eq. (10)

κ_D' screening parameter, defined by eq. (25)

$\lambda_c,\ \lambda_p,\ \lambda_d,\ \lambda_i'$ ionic conductivity of counterion, polyion (per mol of charged groups), co-ion, free (uncondensed) ionic species i

$\lambda_c^\circ,\ \lambda_p^\circ$ limiting ionic conductivity of counterion, polyion (per mol of charged groups)

Λ molar conductivity

$\xi,\ \xi_{str}$ line charge density parameter, structural line charge density parameter

$\xi_{crit},\ \xi_{net}$ critical, net line charge density parameter

σ surface charge density of a particle

$\tau,\ \tau_r$ relaxation time, rotational relaxation time

χ parameter related to the degree of drainage of the coil, defined by eq. (14)

CMC	carboxymethylcellulose (salt)	L	ligand
DE	degree of esterification	PAA	polyacrylate
DNA	deoxyribonucleic acid	PB	polybrene
DS	dextran sulphate	PES	poly(ethylenesulphonate)
FA	fulvic acid	PEI	polyethyleneimine
HA	humic acid	PMA	polymethacrylate
H-CMC	carboxymethylcellulose (acid form)	PMApe	partially esterified
H-PAA	poly(acrylic acid)		poly(methacrylic acid)
H-PMA	poly(methacrylic acid)	PSS	Poly(styrenesulphonate)
M	molar mass	PVP	poly(4-vinylpyridine)
Me	metal(ion)	PVPI	polyvinylpyrrolidone

REFERENCES

1. T. Kurucsev & B.J. Steel, <u>Pure Appl. Chem.</u> <u>17</u>, 149-157 (1967).
2. J.R. Huizenga, P.F. Gregor & F.T. Wall, <u>J. Am. Chem. Soc.</u> <u>72</u>, 2636-2642 (1950).
3. A. Katchalsky, Z Alexandrowicz & O. Kedem in 'Chemical Physics of Ionic Solutions', (B.E. Conway & R.G. Barrada, Eds.), Wiley, New York, p. 295 (1966).
4. G.S. Manning, <u>J. Chem. Phys.</u> <u>51</u>, 924-933 (1969).
5. J.T.G. Overbeek, <u>Pure Appl. Chem.</u> <u>46</u>, 91 (1976).
6. M. Mandel, in 'Encyclopedia of Polymer Science and Engineering', 2nd ed., Vol. 11, Wiley, New York, 739-829 (1988).
7. H. Eisenberg, <u>J. Polymer Sci.</u> <u>30</u>, 47 (1958).
8. W.P.T.J. van der Drift, Ph. D. Thesis, State University Utrecht, The Netherlands (1975).
9. H.G. de Jong, J. Lyklema & H.P. van Leeuwen, <u>Biophys. Chem.</u> <u>27</u>, 173-182 (1987).
10. D.C. Henry, <u>Proc. Royal Soc. London</u>, <u>A 133</u>, 106 (1931).
11. A.L. Loeb, J.T.G. Overbeek & P.H. Wiersema, 'The Electrical Double Layer around a Spherical Colloid', MIT, Cambridge, Mass. (1961).
12. J.T.G. Overbeek & P.H. Wiersema, in 'Electrophoresis', Vol. II, (M. Bier, Ed.) Acad. Press, New York (1967).

13. G.S. Manning, <u>J. Phys. Chem.</u> <u>79</u>, 262-265 (1975).
14. G.S. Manning, <u>J. Phys. Chem.</u> <u>85</u>, 1506-1515 (1981).
15. S.A. Rice & M. Nagasawa, 'Polyelectrolyte Solutions', Academ. Press, New York (1961).
16. C. Beldie, <u>Bul. Inst. Politehnic din Iasi</u> <u>21</u>, 13-20 (1975).
17. J.C.T. Kwak & R.C. Hayes, <u>J. Phys. Chem.</u> <u>79</u>, 265-272 (1975).
18. H. Vink, <u>J. Chem. Soc. Faraday Trans. I</u>, <u>77</u>, 2439-2494 (1981).
19. H.P. Gregor, D.H. Gold & M. Frederick, <u>J. Polymer Sci.</u>, 467-475 (1957).
20. G.S. Manning, <u>Q. Rev. Biophys</u> <u>11</u>, 179-246 (1978).
21. M. Mandel, <u>J. Polymer Sci.</u> C16, 2955-2962 (1967).
22. G.S. Manning, <u>Biopolymers</u> <u>9</u>, 1543-1546 (1970).
23. R.L. Darksus, D.O. Jordan & T. Kurucsev, <u>Trans. Faraday Soc.</u> <u>62</u>, 2876 (1966).
24. F.T. Wall & W.B. Hill, <u>J. Amer. Chem. Soc.</u> <u>82</u>, 5599 (1960).
25. F.M. Tuffile & P. Ander, <u>Macromolecules</u> <u>8</u>, 789-792 (1975).
26. J.F. Thibault & M. Rinaudo, <u>Biopolymers</u> <u>24</u>, 2131-2143 (1985).
27. P. Buchner, R.E. Cooper & A. Wasserman, <u>J. Chem. Soc. London</u>, 3974 (1961).
28. J. Szymczak, P. Holyk & P. Ander, <u>J. Phys. Chem.</u> <u>79</u>, 269-272 (1975).
29. S. Arai & K. Kumada, <u>Geoderma</u> <u>19</u>, 21-35 (1977a).
30. H. Vink, <u>Makromol. Chem.</u> <u>183</u>, 2273-2283 (1982).
31. F.T. Wall & R.H. Doremus, <u>J. Amer. Chem. Soc.</u> <u>76</u>, 1557-1560.
32. D. Adamone, N. Kashkina, M. Pormale & A. Simanovska, <u>Latv. PSR Zinatnu Acad. Vestis</u> <u>3</u>, 317-320 (1979).
33. D. Bratko, N, Celija, D. Dolar, J. Špan, L. Trnkova & V. Vlachy, <u>Makromol.Chem., Rapid Commun.</u> <u>4</u>, 783-788 (1983).
34. G.S. Manning,in 'Polyelectrolytes', Vol. I (E. Sélégny, Ed.), D. Reidel, Dordrecht, pp. 9-37 (1974)
35. S.S. Islam & M.L. Rahman, <u>J. Chem. Tech. Biotechn.</u> <u>29</u>, 419-426 (1979).
36. E.G. Kolawole & J.Y. Olayemi, <u>Macromolecules</u> <u>14</u>, 1050-1054 (1981).
37. R.F.M.J. Cleven, Ph. D. Thesis, Agricultural University Wageningen, The Netherlands (1984).
38. M. Rinaudo & M. Milas, <u>C.R. Acad. Sc. Paris Série C</u> <u>271</u>, 1170-1172 (1970).
39. J. Wallach & M. Hanss, <u>Anal. Biochemistry</u> <u>88</u>, 69-77 (1978).
40. T. Okubo & A. Enokida, <u>J. Chem. Soc. Faraday Trans.</u> <u>1</u>, 1639-1648 (1983).
41. A. Oth & P. Doty, <u>J. Phys. Chem.</u> <u>56</u>, 43-50 (1952).
42. H. Eisenberg & G. Mohan Ram, <u>J. Phys. Chem.</u> <u>63</u>, 671 (1959).
43. J.C.T. Kwak & A.J. Johnston, <u>Can. J. Chem.</u> <u>53</u>, 792 (1975).
44. Y.M. Joshi & J.C.T. Kwak, <u>Biophys. Chem.</u> <u>12</u>, 323-328 (1980).
45. R.E. Nelson & P. Ander, <u>J. Phys. Chem.</u> <u>75</u>, 1691 (1971).
46. D. Dolar, J. Špan & S. Isaković, <u>Biophys. Chem.</u> <u>1</u>, 312-317 (1974).
47. A.M. Kharlamova, N.A. Fedotov & A.V. Ushakov, <u>Soviet Electrochem.</u> <u>8</u>, 637-639 (1972).
48. D.O. Jordan, T. Kurucsev & M.L. Martin, <u>Trans. Faraday Soc.</u> <u>65</u>, 202 (1969).
49. J.C.T. Kwak, G.F. Murphy & E.J. Spiro, <u>Biophys. Chem.</u> <u>7</u>, 379-386 (1978).
50. S. Miyamoto, <u>Biophys. Chem.</u> <u>9</u>, 79-89 (1979).
51. R. Varoqui & U.P. Strauss, <u>J. Phys. Chem.</u> <u>72</u>, 2507-2511 (1968).
52. H. Vink, <u>J. Chem. Soc. Faraday Trans. I</u>, <u>80</u>, 507-514 (1984).
53. T. Okubo, K. Hongyo & A. Enokida, <u>J. Chem. Soc. Faraday Trans.</u> <u>1</u>, 2087-2098 (1984).
54. T. Okubo, <u>Biophys. Chem.</u> <u>11</u>, 425-431 (1980).
55. B.C. Bonekamp & J. Lyklema, <u>J. Colloid Interface Sci.</u> <u>113</u>, 67-75 (1986).
56. S. Oden, <u>Ber. Deut. Chem. Gesellsch.</u> <u>35</u>, 651-660 (1912).
57. B. Chatterjee & S. Bose, <u>J. Colloid Sci.</u> <u>7</u>, 414-427 (1952).
58. H. van Dijk, <u>Sci. Proc. Royal Dublin Soc. Ser. A 1</u>, 163-176 (1960).
59. S.K. Banerjee, S.C. Das & B. Das, <u>J. Indian Chem Soc.</u> <u>53</u>, 186-188 (1976).
60. S. Arai & K. Kumada, <u>Geoderma</u> <u>19</u>, 307-317 (1977b).
61. N. Ram & K.V. Raman, <u>Pedologie</u> <u>33</u>, 137-145 (1983).
62. S.O. Johnson & W.S. Hnojewyj, <u>Proc. N.D. Acad. Sci.</u> <u>20</u>, 180-187 (1986).
63. D.S. Gamble, <u>Can. J. Chem.</u> <u>48</u>, 2662-2669 (1970).
64. N.C. Lockhart, <u>Clays and Clay Minerals</u> <u>29</u>, 413-422 (1981a).
65. M.K. Pal & M. Chaudhurih, <u>Makromolekulare Chemie</u>, 151-160 (1970).
66. T. Corner, <u>Colloids and Surfaces</u> <u>3</u>, 119-129 (1981).
67. M. Rinaudo & M. Daune, <u>J. Chimie Phys.</u> <u>63</u>, 1753-1760 (1967).
68. M. Nagasawa, in 'Polyelectrolytes', Vol. I (E. Sélégny, Ed.), D. Reidel, Dordrecht, pp. 57-77 (1974)
69. J. Buffle, 'Complexation reactions in aquatic systems', Ellis Horwood, Chichester (1988).
70. W. Flaig, H. Beutelspacher & E. Rietz, in:'Soil Components', Vol. 1, (Gieseking, J.E., Ed.), Springer, Berlin, 1-211 (1975).
71. N.C. Lockhart, <u>Clays and Clay Minerals</u> <u>29</u>, 423-428 (1981b).
72. M. Schnitzer & S.I.M. Skinner, <u>Soil Sci.</u> <u>96</u>, 86-93 (1963).
73. B.G. Gaberman & A.S. Litovko, <u>Chimija Tverdogo Topliva, Moskva</u> <u>5</u>, 34-39 (1972).
74. G. Muller, C Ripoll & E. Selegny, <u>Eur. Polymer J.</u> <u>7</u>, 1373-1392 (1971).
75. S.A. Jones, D.M. Goodall, A.N. Cutler & I.T. Norton, <u>Eur. Biophys. J.</u> <u>15</u>, 185-191 (1987).
76. N.Th.M. Klooster, F. van der Touw & M. Mandel, <u>Macromolecules</u> <u>17</u>, 2078-2086 (1984).
77. T. Okubo, <u>Macromolecules</u> <u>22</u>, 1818-1821 (1989).
78. H.G. de Jong & H.P. Van Leeuwen, <u>J. Electroanal. Chem.</u> <u>234</u>, 1-16, 17-29 (1987).
79. H.P. van Leeuwen, R.F.M.J. Cleven & J. Buffle, <u>Pure & Appl. Chem.</u> <u>61</u>, 255-274 (1989).