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Conductometric analysis of the competition between monovalent and divalent counterions in their interaction with polyelectrolytes

Hans G. de Jong, Johannes Lyklema and Herman P. van Leeuwen

Laboratory for Physical and Colloid Chemistry, Agricultural University, De Dreijen 6, 6703 BC Wageningen, The Netherlands

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A procedure is described for the analysis of the conductivity of solutions of anionic polyelectrolytes in which both mono- and divalent counterions are present. The method is based on analysis of the relation between the overall conductivity of the system and the conductivity of the individual monovalent cations which are only electrostatically (non-specifically) bound. The system is described in terms of the two-state approach, implying that the counterions are considered to be either fully bound to the polyion or completely free. The potentialities of the proposed method are explored by studying solutions of alkali polyacrylates with and without added zinc nitrate at several alkali nitrate concentrations. The results give a picture of the composition of the counterionic atmosphere around the polyion in systems with both mono- and divalent counterions present. To a certain degree, the divalent ion Zn(II) was found to be bound quantitatively by the polyion. The composition of the counterionic atmosphere around the polyion was largely independent of alkali nitrate concentration when the latter was present in not too large an excess with respect to both Zn(II) and the charged monomers.

1. Introduction

Conductometry has become an important tool in the analysis of properties of polyelectrolyte solutions [1–5]. The properties which have been studied thus far are the concentration dependence of the conductivity of polycarboxylates [1] and polystyrenesulfonates [2], the temperature dependence of the conductivity of alkali polycarboxylates and the influence of the degree of neutralization [1]. Furthermore, the influence of the nature of the counterion on the conductivity of polyelectrolyte solutions has been studied [1,3,5] and a detailed investigation of the conductivity of alkali polymethacrylates in the presence of the corresponding alkali bromide has been performed [3].

Recently, conductometric titration was suggested as a tool for investigating the interaction of polyelectrolytes with heavy metals [4,6]. Such an approach is promising because of the fairly easy way in which the automation of equipment is achieved. Furthermore, the transport properties of polyelectrolyte solutions are more sensitive to the polymer configuration than the equilibrium properties [2], which means that in principle more information can be obtained from measurements of transport properties than those of equilibrium. In the analysis of Cleven [4], the interpretation remained more or less qualitative.

In another study, calculations of the overall conductivity were given for polysulfonic acids partly neutralized by Mg^{2+} [7]. However, competition between monovalent and divalent counterions in their interaction with the poly acids has not yet been assessed conductometrically nor was the behavior of the bound fractions of the two types of

Correspondence address: H.G. de Jong, Laboratory for Physical and Colloid Chemistry, Agricultural University, De Dreijen 6, 6703 BC Wageningen, The Netherlands.

counterions involved. The present work is aimed at a systematic analysis of the conductivity of mixed-valency counterion-polyelectrolyte systems. This involves the quantification of bound (or free) fractions of the counterions involved, including competition in their interaction with the polyion. Such an analysis is a basic step in the further investigation of these complex systems. The analysis is based on the two-state approach, i.e., counterions are assumed to be found either in some kind of bound state or are entirely free, in the sense that they are not at all influenced by the electric field around the polyion. Such a two-state approach is common in polyelectrolyte theory [7–9]. In this study alkali polyacrylates are chosen as the model systems. They are titrated with zinc nitrate. The results are compared with radioactive counterion tracer diffusion data.

2. Theory

In this section the interpretation of the conductometric titrations of an aqueous polyelectrolyte solution with a solution of a divalent metal salt in systems with or without added 1 : 1 salt is described. First, the case in the absence of added 1 : 1 salt will be treated.

2.1. Conductivity of mixed-valency counterion-polyelectrolyte solutions

According to the two-state approximation [8], the specific conductivity of a polyelectrolyte solution, which consists of negatively charged polyions together with several types of counterions and co-ions, may be written as:

$$\kappa = \sum_i f_i \lambda_i^\circ C_i + \sum_j (\lambda_-)_j (C_-)_j + f_\mathrm{p} \lambda_\mathrm{p} C_\mathrm{p} \qquad (1)$$

where

C_i, C_p and $(C_-)_j$ denote the total concentrations of counterions of type i, deprotonated groups on the polyion and co-ions of type j, respectively;
λ_i° the molar conductivity of counterions of type i in pure solvent;
λ_p and $(\lambda_-)_j$ the molar conductivities of the polyion (per mol deprotonated monomers) and co-ions of type j, respectively;
f_i and f_p the fractions of conductometrically free counterions [6,10] of type i and deprotonated groups, respectively; and
$f_i \lambda_i^\circ C_i$ and $(\lambda_-)_j (C_-)_j$ the contributions to the total conductivity of counterions of type i and co-ions of type j, respectively.

Bound ions are defined as ions having the same mobility as the polyion. Upon binding of a counterion, the contributions to the overall conductivity of both the bound ion and an electrically equivalent amount of deprotonated monomers are annihilated.

The relation between θ_i, the number of bound counterions per deprotonated monomer, and f_i reads:

$$\theta_i = \frac{z_i (1 - f_i) C_i}{C_\mathrm{p}} \qquad (2)$$

and f_p is then written as:

$$f_\mathrm{p} = 1 - \sum_i \theta_i \qquad (3)$$

Applying eqs. 1–3 to the titration of a salt-free polyelectrolyte solution with a 2 : 1 salt, the specific conductivity of the mixture may, for any stage of the titration, be written as:

$$\kappa(C_2) = f_1(\lambda_1^\circ + \lambda_p) C_1 + \left[f_2 \lambda_2^\circ - 2(1 - f_2)\lambda_\mathrm{p} \right] C_2 + \lambda_- C_- \qquad (4)$$

The subscripts 1 and 2 refer to monovalent and divalent counterions, respectively. Note that in the salt-free case $C_\mathrm{p} = C_1$. The contributions of H^+ and OH^- to the total conductivity are ignored, because under the conditions of our experiments with poly (acrylic acid), (PAA) their concentrations were negligible. The molar conductivity of the solution may be represented as:

$$\Lambda = \kappa(C_2)/(C_\mathrm{p} + C_-) \qquad (5)$$

2.2. The conductivity excess function

The conductivity excess was shown to be a suitable parameter for representing conductometric titration data [4]. It is defined as the difference between the specific conductivity of a metal/polyelectrolyte system and the sum of the conductivities of the metal salt and polyelectrolyte solution before mixing. For the case of titration with a divalent electrolyte:

$$\Delta\kappa_T = -\{\kappa(C_2) - [\kappa(C_2=0) + \kappa_{bl}(C_2)]\} \qquad (6)$$

The sign is chosen for convenience such that association phenomena give rise to a positive $\Delta\kappa_T$. Here, $\kappa_{bl}(C_2)$ is the specific conductivity of a solution of the 2 : 1 salt:

$$\kappa_{bl}(C_2) = \lambda_2^\circ C_2 + \lambda_-^\circ C_- \qquad (7)$$

In eq. 6, $\kappa(C_2 = 0)$ represents the specific conductivity of the polyelectrolyte solution without added 2 : 1 salt. It is equal to:

$$\kappa(C_2 = 0) = f_{1,0}(\lambda_1^\circ + \lambda_p)C_1 \qquad (8)$$

where $f_{1,0}$ is the fraction of conductometrically free monovalent counterions in the polyelectrolyte solution without added 2 : 1 salt. To a good approximation λ_- is not influenced by the electric field around the polyion [3]. Combination of eqs. 4 and 6–8 yields:

$$\Delta\kappa_T = (f_{1,0} - f_1)(\lambda_1^\circ + \lambda_p)C_1 + (\lambda_2^\circ + 2\lambda_p)(1 - f_2)C_2 \qquad (9)$$

Generally, polyanions prefer binding of divalent over monovalent counterions [11]. This allows one to interpret the first term on the right-hand side of eq. 9 as the conductivity gain due to the release of bound monovalent ions by binding of divalent ions. The second term represents the conductivity loss due to divalent counterion binding. It is obvious that the parameter f_1 depends on C_2. For a complete analysis of the titration data in terms of conductivity excesses, it is necessary to determine the relationship between these two parameters. Furthermore, at every point of the titration λ_p must be known.

2.3. Determination of f_1 and λ_p in systems with and without added 1 : 1 salt

From eq. 8 a linear relationship is expected between the molar conductivity of a polyelectrolyte and λ_1° if $f_{1,0}$ is a constant. This is the case if, upon a change in the nature of the monovalent cation, its extent of binding remains unaltered. This situation is expected to occur if the counterions are purely electrostatically (i.e., non-specifically) bound. The linearity sought has been shown to apply for Li, Na and K polyacrylates at the millimolar level [3]. Therefore, in that case it is possible to evaluate $f_{1,0}$ together with λ_p from a plot of Λ vs. λ_1° for Li, Na and K polycarboxylate solutions. The slope and intercept of the straight line obtained in this way equal $f_{1,0}$ and $f_{1,0}\lambda_p$, respectively.

When the competition between the alkali metal counterions and the divalent counterion is not specific and λ_p remains unaltered (see section 4.2), the plot of Λ vs. λ_1° will remain linear as in the absence of the divalent counterion. Therefore, the procedure described above remains applicable and f_1 can be determined from the slope of the plot of Λ vs. λ_1°.

In the presence of an added 1 : 1 salt essentially the same procedure can be used when the additivity rule applies. According to this rule, the overall specific conductivity of a polyelectrolyte solution may be written as the sum of independent contributions of the specific conductivities of the added 1 : 1 salt and the polyelectrolyte system [3]. The additivity rule was found to be valid for several properties of polyelectrolyte solutions [3,12,13]. The specific conductivity of the polyelectrolyte system is then:

$$\kappa = \kappa_{total} - \kappa_a \qquad (10)$$

where κ_a is the specific conductivity of the added 1 : 1 salt. From κ, the molar conductivity of the polyelectrolyte system is easily calculated and the relation between Λ and λ_1° is analyzed. In this case the slope is equal to $(1 - \theta_1)$ rather than to f_1. For a salt-free system $(1 - \theta_1)$ is of course equal to f_1 according to eq. 3.

3. Experimental

Conductivity measurements were performed with a Wayne Kerr B 905 automatic precision bridge, equipped with and IEEE interface allowing computer control. The conductometric cell was a WTW model LTA 01 with a cell constant of 0.109 cm^{-1}. The cell constant was periodically calibrated. All conductivity measurements were performed at a frequency of 10 kHz. A Metrohm type 655 automatic buret was used to add 50- or 100-μl aliquots of 0.05 M $Zn(NO_3)_2$ solution to 50 ml of sample solution. The titration was controlled by an HP 85 A (Hewlett Packard) personal computer programmed with BASIC. The temperature inside the titration vessel was maintained at $25.00 \pm 0.02°C$ by a Julabo F10 thermostat. The automatic buret and titration vessel were kept in an air temperature controlled environment maintained at $25.0 \pm 0.5°C$ with a home-made air thermostat. Prior to measurements, samples were stirred for about 1 h to achieve thermal equilibrium, while purging with CO_2-free, water-saturated N_2 at 25°C. After every addition the sample was stirred and purged with N_2 for about 5 min. During the actual measurement N_2 was passed over the solution. All samples were prepared using demineralized tap water, produced by a Millipore Super-Q reverse osmosis system. After removing CO_2, the conductivity of this water never exceeded 0.6 $\mu S\ cm^{-1}$.

All chemicals used were of analytical grade. Polyacrylic acid (PAA, average molecular mass 230 kDa) was obtained from BDH Chemicals and used without further treatment.

For fully deprotonated PAA, the structural charge density parameter ξ, which is defined as the ratio between the Bjerrum length (l_B) and the average distance between the charged monomers b, under the present experimental conditions is $\xi = l_B/b = 2.85$. For a particular degree of neutralization α_n, ξ becomes $\alpha_n l_B/b$.

Solutions of alkali polyacrylates were prepared

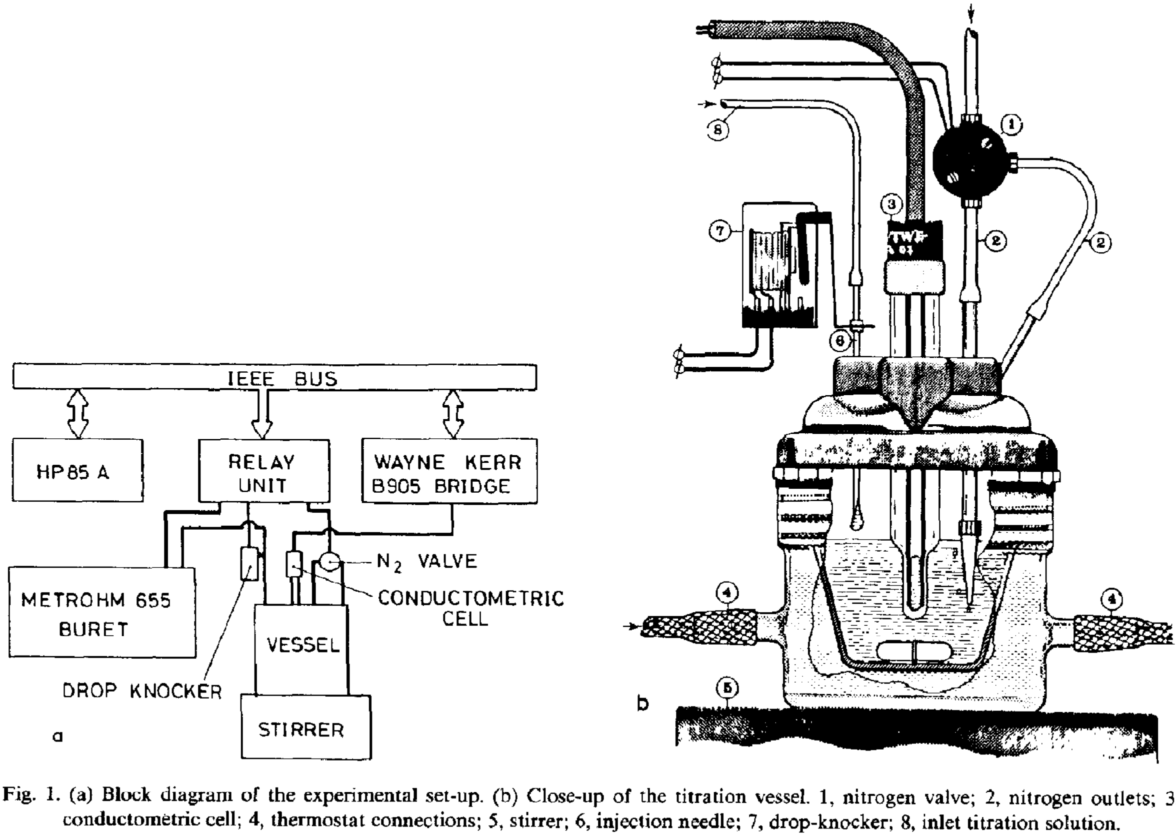

Fig. 1. (a) Block diagram of the experimental set-up. (b) Close-up of the titration vessel. 1, nitrogen valve; 2, nitrogen outlets; 3, conductometric cell; 4, thermostat connections; 5, stirrer; 6, injection needle; 7, drop-knocker; 8, inlet titration solution.

by neutralizing the poly acid with the appropriate hydroxide solution to the desired degree of neutralization.

The set-up is shown schematically in fig. 1a and b. The precision of the measured conductivity steps achieved with this system was typically 0.2% for 50- and 100-μl additions of 0.05 M $Zn(NO_3)_2$ to water on two consecutive days.

4. Results and discussion

4.1. Conductance of alkali polyacrylate solutions

In fig. 2 plots are shown of the molar conductivity of several alkali polyacrylates vs. that of the alkali ions in pure solvent at different concentrations of Zn(II). The linear relationship between Λ and λ_1° is obvious at all Zn(II) concentrations. This means that the non-specific nature of the interaction of alkali metal ions and the polyacrylate anion, as previously found by Eisenberg [1] and Van der Drift [3] for the polymethacrylates, persists during their competition with Zn^{2+} for binding by the polyion. Using eq. 5 this result enables one to calculate f_1 at any stage of titration of alkali polyacrylate solutions with a zinc salt solution. The f_1 value in blank alkali polyacrylate solution, with [PAA] = 2.50 mM and $\alpha_n = 0.8$ was found to be 0.47 ± 0.02 which is in excellent agreement with the results obtained from radioactive tracer diffusion measurements, performed by Ander and Kardan [13]. These results are in accordance with theoretical expectations [7,8]. It may be noted that with this f_1 value the net charge density parameter ξ_{net} is not far from unity, in accordance with Manning's predictions [11].

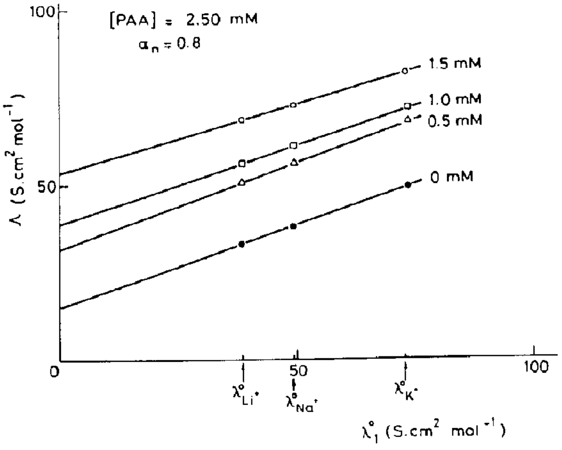

Fig. 2. Plot of the molar conductivity of alkali polyacrylate solutions at the indicated zinc concentrations vs. molar conductivity of the corresponding monovalent counterion.

As outlined in section 2, λ_p can be evaluated from the Λ vs. λ_1° plot. This procedure yields $\lambda_p = 30 \pm 5$ S cm^2 mol^{-1} for a solution with [PAA] = 2.50 mM and $\alpha_n = 0.8$. Anticipating the analysis of the relationship between f_1 and C_2/C_1 it was found that an alternative procedure is available, yielding a more precise value for λ_p: extrapolation of f_1 vs. C_2/C_1 (fig. 4) to zero yielded $f_{1,0} = 0.469 \pm 0.005$. Using this value, λ_p was calculated from the molar conductivity of Li, Na and K polyacrylate solutions. An average value of 31.1 ± 0.8 S cm^2 mol^{-1} was obtained. This procedure was used in all other evaluations of λ_p.

4.2. Behavior of λ_p

In table 1, λ_p values are listed for different degrees of neutralization. An increase in λ_p with decreasing α_n is observed. Qualitatively the same behavior was found for polymethacrylates [3] and carboxymethylated hydroxyethylcellulose [14]. At relatively high salt concentrations (0.1 M NaCl) this trend was reversed for sodium polyacrylate as

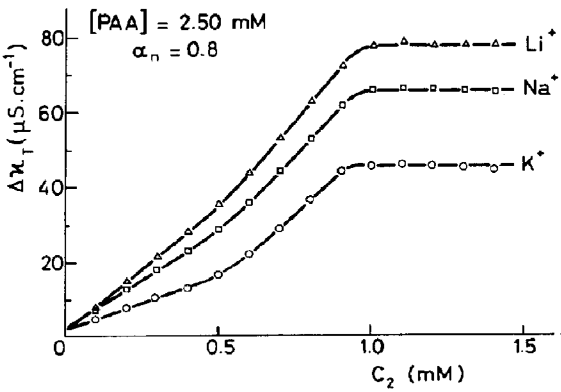

Fig. 3. Conductivity excess curves of three alkali polyacrylate solutions as a function of the concentration of Zn(II). Standard deviation of $\Delta\kappa_T$ values was typically about 0.4 μS cm^{-1}.

reported by Noda et al. [15]. Probably conformational aspects play a role in this matter in the sense that the frictional coefficient of the polyion is dependent on the charge density. In the salt-free case, highly charged polyions may have a cylindrical shape, whereas lower charged polyions have a more compact worm-like chain conformation [16] with a lower frictional coefficient. The λ_p data in table 1, which will be further discussed below, suggest that the change in frictional drag dominates the change in electrical force on the polyion when changing the charge density. When a large amount of a 1 : 1 salt is added, the dimensions of the polyion become smaller [16] and variation in frictional drag is not as important as in the salt-free case, which probably accounts for the observed differences. For $\alpha_n = 0.8$, the dependence of λ_p on concentration of added 1 : 1 salt is presented in table 2. A large decrease in λ_p with increasing concentration of added 1 : 1 salt is observed. The same trend, although less dramatically, was found for alkali polymethacrylates [3].

Fig. 3 shows some typical conductivity excess curves for alkali polyacrylates with a highly charged polyion. It appears to be a general experience that the first data points of the conductivity excess curves form a straight line (statistics for Li polyacrylate, first five data points $R^2 = 1.000$; $F = 10\,899$). The same is true for certain data points for higher concentrations of added zinc nitrate (statistical data for Li polyacrylate, next four data points $R^2 = 1.000$; $F = 6485$. Finally, the curves become horizontal. The linear dependence of the conductivity excess on C_2 implies that $\Delta\kappa_T$ is independent of λ_p. There are two circumstances in which this independence could be established. The first is if $(f_{1,0} - f_1)C_1 \approx -2(1 - f_2)C_2$, which is the case when, upon binding of one Zn^{2+}, two bound monovalent ions are released. The second option is that λ_p is constant during titration. Analysis of data on the basis of the first assumption yields values for $1 - f_2$ that systematically were in the range 1.2–1.5, which is clearly impossible. Therefore, it is concluded that λ_p is essentially constant during titration. It is well known from theory that λ_p may be dependent on λ_c° [17,18]. From the expression for the electric mobility of a polyion derived by Imai and Iwasa [18], using a value of the order of 10^{12} kg mol^{-1} s^{-1} for the frictional coefficients of counterions (calculated from diffusion coefficients [19]) and a frictional coefficient of the uncharged polyion within the range 10^{14}–10^{15} kg mol^{-1} s^{-1} (ref. 14 and unpublished results of this laboratory), the electric mobility of the polyion is indeed found to be essentially independent of the type of counterion.

If it is true that in the course of the titration under the present experimental conditions no change in dimensions occurs, the contribution to the electric mobility of an individual charged group on the polyion should not be affected by addition of Zn^{2+}. Thus, if the solvent properties do not change during the titration, the only parameter left to affect the net conductivity of the polyion is its apparent charge. Hence, its net conductivity for any point during the titration is f_p times the λ_p found in blank polyelectrolyte solutions. Therefore, λ_p in eqs. 2,4 and 9 is the λ_p calculated from blank polyelectrolyte solutions. This reasoning is supported by dynamic light scattering experiments performed by Magdelénat et al. [20] who found a linear decrease in overall mobility of the polyionic species, when titrating Na chondroitin sulfate with Ca^{2+}. This linear decrease indicates that the mobility of the polyionic species is, at least in part of the titration, only dependent on its apparent charge. The same type of behavior of λ_p was tacitly implied by Thibault and Rinaudo [21] in their calculations concerning conductivity data of a polyelectrolyte solution with only divalent counterions present.

Finally, from fig. 3 it is clear that the $\Delta\kappa_T$ curves show a small intercept. Strictly they should pass through the origin. This observation may suggest that during the titration λ_p may be a constant, which is different from the initial value. However, analysis of the intercept in terms of this concept yields a λ_p value which is not significantly different from the starting value. Furthermore, calculation of $1 - f_2$ from the slope of the linear parts of the conductivity excess curves yields the same value as obtained by calculation using the $\Delta\kappa_T$ values point by point. This suggests that the observed intercepts are of incidental nature and do not seriously affect the analysis.

4.3. Analysis of conductivity excess curves

As demonstrated in fig. 3, the conductivity excess curves of the alkali polyacrylates show similar shapes. Using the dependence of f_1 on C_2 as derived from Λ, λ_1° plots and taking for λ_p its value in blank polyelectrolyte solutions, the fraction of bound Zn^{2+} can be calculated from the conductivity excess. In fig. 4 the resulting f_1 and f_2 values are shown for different C_2/C_1 ratios. The f_2 values were calculated using eq. 9 and are average values for the three alkali polyacrylate solutions. Error bars indicate the standard errors. As is inferred from fig. 4 f_2 is practically zero up to $C_2/C_1 = 0.45$, or in other words, the added Zn^{2+} is practically quantitatively bound over the major part of the titration. Similarly to the conductivity excess curves, the plot of f_1 vs. C_2/C_1 shows two linear parts and a more or less horizontal part. The first linear part is between $C_2/C_1 = 0$ and 0.25 (with statistics: $n = 6$, $R^2 = 0.999$, $F = 4000$) and the second between $C_2/C_1 = 0.30$ and 0.50 ($n = 5$, $R^2 = 0.998$, $F = 951$). The intersection of these two linear parts coincides, within 1%, with that of the corresponding part of the conductivity excess curve (fig. 3). At this stage of titration ξ_{net} ($= f_p \xi$) is about 0.5. It should be noted that the monovalent ions are not completely free at this stage. In the region around $C_2/C_1 = 0.50$ the behavior of the polyelectrolyte system is less clear-cut. Here, the conductivity excess curves are not linear and changes in the dimensions of the polyion may occur, implying a change in λ_p. Consequently, beyond $C_2/C_1 \approx 0.50$ the fraction of free divalent ions cannot be calculated exactly. The two dashed parts of the f_2 curve represent two extremes: the upper curve is calculated neglecting any additional binding of Zn^{2+}, whereas the lower one is calculated assuming a constant λ_p. The first approach may overestimate f_2, while the second is an underestimation. However, it is obvious that both curves approach each other. Furthermore, for $C_2/C_1 > 0.55$, f_1 becomes independent of C_2/C_1. The observation suggests that binding of Zn^{2+} ceases beyond $C_2/C_1 = 0.55$. In this region ξ_{net}, like f_2, cannot be calculated exactly; estimations on the basis of limiting cases yield a value between 0.05 and 0.16. The general conclusion is

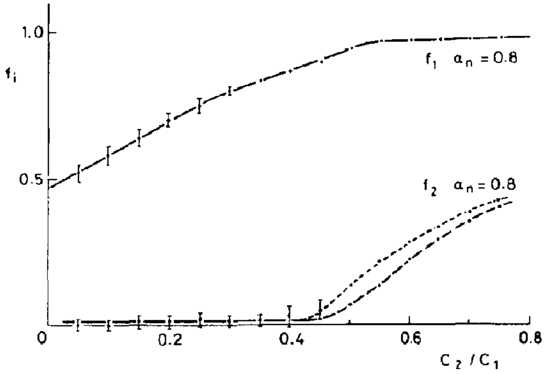

Fig. 4. Plots of f_1 and f_2 vs. the ratio C_2/C_1 for the alkali polyacrylate of fig. 3. Typical standard deviation in f_1 values is 0.01 and in f_2 values 0.04.

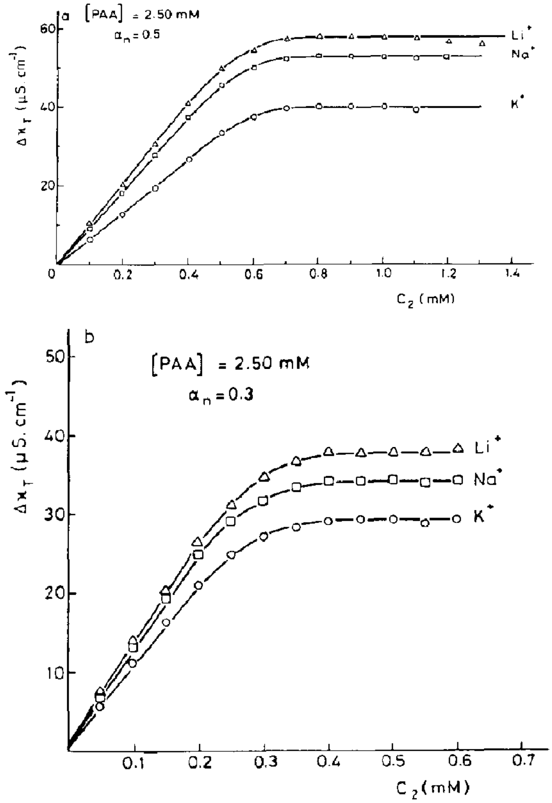

Fig. 5. Conductivity excess curves of alkali polyacrylate solutions as a function of the concentration of Zn(II). Standard deviations; see fig. 3.

that Zn^{2+} is completely bound at charge densities below 0.5.

In fig. 5 conductivity excess curves are shown for $\alpha_n = 0.3$ and $\alpha_n = 0.5$. As compared to the corresponding curves obtained for $\alpha_n = 0.8$ the kinks in the rising part are absent. In the curved parts of the plots, calculation of f_2 – using the value for λ_p obtained by conductance measurements in blank polyelectrolyte solutions – led to inconsistent results. This suggests that changes in the dimensions of the polyion, affecting its molar conductivity, may occur in the curved regions. Without knowledge of λ_p in these regions, conductivity data cannot be interpreted quantitatively. Here additional experiments are necessary to obtain λ_p. Generally, it appears that only the linear parts of the conductivity excess curves may be analyzed successfully.

In fig. 6, θ_1 and θ_2 are plotted vs. the ratio C_2/C_1 for $\alpha_n = 0.3$, 0.5 and 0.8. Taking into account an experimental error of typically 0.04, the bound fraction of Zn(II) does not vary significantly with the degree of neutralization. Under the present conditions, all added Zn^{2+} is quantitatively bound at any degree of neutralization of the polyion.

4.4. Competition between monovalent and divalent counterions

According to Poisson-Boltzmann calculations a 1 : 1 exchange of bound monovalent counterions against added divalent counterions should be expected for titration of a polyelectrolyte solution with a divalent salt [22]. The same was predicted by Miyamoto and Imai [23], who gave an analysis of the competition between mono- and divalent counterions based on the Poisson and Fokker-Planck equations. Condensation theory predicts that two bound monovalent counterions will be exchanged for one added divalent counterion [13,24]. In the first part of the titration, i.e., $0 < C_2/C_1 \leqslant 0.25$, the exchange ratio $r = -d\theta_1/d(1-f_2)C_2$ was 1.13 ± 0.04 for $\alpha_n = 0.8$, which is not too far from a 1 : 1 exchange. In the second part of the titration, i.e., $0.30 \leqslant C_2/C_1 \leqslant 0.45$, fewer bound monovalent counterions are displaced per bound divalent ion. Here, $r = 0.64 \pm 0.05$. Possibly in the first part of the titration counterion exchange takes place in the immediate vicinity of the polyion, which is the case that Guéron and Weisbuch [22,25] dealt with, whereas in the second part exchange occurs in a region where the monovalent counterions are not too close to the polyion, but are nevertheless restricted in mobility. The existence of such a region of restricted mobility, together with one close to the polyion and another in which the counterions are not influenced by the electric field of the polyion has been advocated by Magdélenat et al. [20].

For $\alpha_n = 0.5$ a 1 : 1 exchange for bound monovalent counterions and added divalent counterions is found over the entire accessible range. The same results were obtained for Ca^{2+}/Na^+ competition in aqueous solutions of a maleic acid copolymer studied by potentiometry [26]. At $\alpha_n = 0.3$, how-

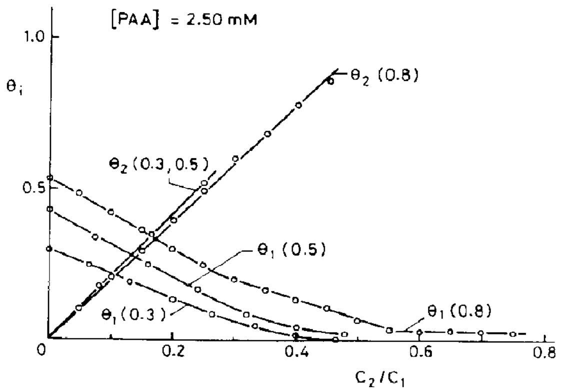

Fig. 6. Plots of θ_1 and θ_2 vs. the ratio C_2/C_1 for several degrees of neutralization. Typical standard deviation in θ_1 values is 0.01 and in θ_2 values 0.04.

Table 1

Bound fractions and conductivity data of alkali polyacrylate solutions at different degrees of neutralization

[PAA] = 2.50 mM in the presence of $Zn(NO_3)_2$.

	α_n		
	0.3	0.5	0.8
$1-f_{1,0}$	0.305 ± 0.005	0.429 ± 0.003	0.531 ± 0.005
$1-f_2$	1.09 ± 0.04	1.09 ± 0.05	0.99 ± 0.02
r	0.74 ± 0.05	1.01 ± 0.07	1.13 ± 0.04 [a] 0.64 ± 0.04 [a]
λ_p (S cm^2 mol^{-1})	45.6 ± 0.8	39.8 ± 0.7	31.1 ± 0.9

[a] See text.

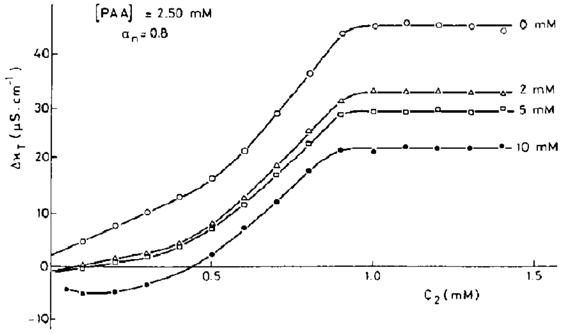

Fig. 7. Conductivity excess curves of potassium polyacrylate solutions for the indicated potassium nitrate concentrations, as a function of the concentration of Zn(II). In the worst case (10 mM KNO_3) the standard deviation of $\Delta\kappa_T$ values was typically about 1 μS cm^{-1}.

Table 2

Bound fractions and conductivity data of alkali polyacrylate solutions at different concentrations of added alkali nitrate $[NO_3^-]_a$

[PAA] = 2.50 mM and $\alpha_n = 0.8$ in the presence of $Zn(NO_3)_2$.

	$[NO_3^-]_a$ (mM)		
	0	2	5
$\theta_{1,0}$	0.531 ± 0.005	0.510 ± 0.006	0.504 ± 0.008
$1 - f_2$	0.99 ± 0.02	0.94 ± 0.06	0.95 ± 0.05
r	1.13 ± 0.04	1.21 ± 0.08	1.19 ± 0.09
	0.64 ± 0.04	0.67 ± 0.05	0.63 ± 0.08
λ_p(S cm^2 mol^{-1})	31.1 ± 0.9	17 ± 2	11 ± 2

ever, more Zn^{2+} needs to be bound to release the same amount of bound monovalent ions. The results of the analysis given so far are summarized in table 1.

4.5. The case with an added 1 : 1 salt

In fig. 7 the conductivity excess curves for potassium polyacrylate at several KNO_3 concentrations are shown. Up to 5 mM KNO_3 the shapes of the conductivity excess curves are similar. From about 10 mM, significant deviations from this shape are observed. At this KNO_3 concentration the conductivity excess curves were not easy to interpret and evaluation as outlined in section 2 led to inconsistent results. Nevertheless, it appears that in the beginning of the titration the added Zn^{2+} is not completely bound in contrast to the case for a low concentration of 1 : 1 electrolyte. Perhaps, at the high salt concentrations binding of monovalent counterions is favored by their excess. This behavior was also reported by Magdelénat et al. [27] and Ishikawa [28].

In table 2 results for alkali polyacrylates with a degree of neutralization of 0.8 at several salt concentrations below 10 mM are summarized. It can be seen that the composition of the counter charge around the polyion is not influenced by the alkali nitrate concentration provided it remains below 5 mM. The internal consistency of the results for $(1 - \theta_{1,0})$ is confirmed by the very good agreement with the results obtained from radioactive diffusion measurements by Ander et al. [29]. These findings further support the assumed additivity rule for the conductivity of polyelectrolyte solutions. The insensitivity of the fraction of bound divalent counterions for a limited excess of added 1 : 1 salt was also found by Magdelénat for Sr^{2+} in a solution of Na chondroitin sulfate and NaCl using radioactive tracer diffusion measurements [27].

For the case of an excess of 1 : 1 salt, the Poisson-Boltzmann equation was numerically integrated. The exchange ratio r was found to be 0.8 for a cylindrical charge distribution with a charge density corresponding to PAA with $\alpha_n = 0.8$. For low charge densities the calculated r decreases to about 0.7. These preliminary computations are in qualitative agreement with the observed tendency of r to decrease with decreasing charge density (see table 2). It is curious in this respect that, in the conductometric part of their study on the binding of Zn^{2+} to polymethacrylate anions in 10 mM KNO_3, Kolawole and Olayemi [6] paid no attention at all to the release of bound monovalent counterions upon addition of divalent counterions.

5. Conclusion

Conductometry is a valuable tool in the analysis of ion distributions in metal/polyelectrolyte systems. For the zinc/polyacrylate systems in

$LiNO_3$, $NaNO_3$ and KNO_3 solutions, the relationship between Λ and λ_1° as well as that between the conductivity excess and C_2 was linear. This allows the computation of the bound fractions of both the monovalent and divalent counterions. Up to a certain concentration level, the composition of the counterionic atmosphere around the polyion was insensitive to the added alkali nitrate. The M^+/M^{2+} exchange ratio r shows a discrete behavior and it was found to be dependent on both the degree of neutralization of poly(acrylic acid) and the amount of bound divalent counterions. For high α_n, r is close to unity over a particular range of M^+/M^{2+} ratios.

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