of dissociation, $0.1 \leq \alpha \leq 0.25$, which results in a small, compact particle where the macromolecular chain is perhaps in a collapsed state. Although the titration curves of PAA in methanol in the presence of Li^+ reveal specific solvent effects that are not understood on a purely electrostatic basis alone, no evidence of a conformational transition analogous to the one observed for Na^+ has been found so far.

In a subsequent paper other experimental techniques will be used to study the titration behavior of PAA in methanol in the presence of both kinds of counterions in order to find out whether or not these preliminary conclusions can be sustained.

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Registry No. PAA, 9003-01-4; methanol, 67-56-1; lithium, 7439-93-2; sodium, 7440-23-5.

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Solvent Effects in Polyelectrolyte Solutions. 2. Osmotic, Elastic Light Scattering, and Conductometric Measurements on (Partially) Neutralized Poly(acrylic acid) in Methanol

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ABSTRACT: Osmotic pressure, elastic light scattering, and conductance measurements have shown that the behavior of partially neutralized poly(acrylic acid) (PAA) in methanol at room temperature is different in the presence of Na^+ from that in the presence of Li^+ as counterion, in agreement with what was found by potentiometric and viscosimetric titrations. The results seem to be consistent with the occurrence of a conformational transition of PAA around 20% neutralization by sodium methoxide. After this transition the scattering intensity was too high for further analysis, but the results of the two other techniques indicated a strong reduction of the net charge of the NaPAA/PAA particle during the transition and a low value of that charge thereafter. Neutralization of PAA by lithium methoxide showed a more gradual reduction of the net charge. For these solutions neither the osmotic coefficient nor the reduced conductivity can be properly understood by current polyelectrolyte theories emphasizing electrostatic interactions only. From low-angle elastic light scattering data the osmotic coefficients of the LiPAA/PAA solutions could easily be obtained and were found to be in excellent agreement with the osmotic coefficients derived directly from osmotic pressure measurements.

I. Introduction

In the previous paper (to be called part 1) it was shown that the potentiometric and viscosimetric titration of poly(acrylic acid) (PAA) in methanol at room temperature with CH_3ONa gives qualitatively different results from that with CH_3OLi. The experimental evidence suggests that in the presence of Na^+ as the counterion, PAA molecules undergo a conformational transition in the range $0.10 < \alpha < 0.25$ (α being the degree of dissociation of the polyacid) from a more or less expanded coil to a compact, perhaps collapsed, particle, a transition not observed in water under the same experimental conditions. Although the results in methanol with Li^+ as compared to those of PAA in water irrespective the exact nature of the alkaline counterion cannot be understood solely by classic polyelectrolyte theory using an increase in the electrostatic interactions

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between polyion and counterions (due to the much lower relative permittivity ϵ of methanol with respect to water), the experimental evidence did not reveal the same kind of conformational transition for PAA in methanol neutralized by CH_3OLi.

It is interesting to compare these results with results obtained by other physical techniques applied to PAA in methanol using titrations with both bases. Here experimental data obtained by osmometry, elastic light scattering, and conductometry will be presented that will be shown to be consistent with the conclusions drawn in part 1.

Polyelectrolyte solutions without additional salt are in general characterized by rather low values of the osmotic coefficient g even at a moderate linear charge density. The osmotic coefficient expresses the ratio between the actual osmotic pressure Π and the osmotic pressure of the solution according to the vant Hoff expression for the ideal osmotic pressure, $\Pi_{id} = RTC_p(P^{-1} + \alpha)$, where C_p stands for the monomolar concentration of the macromolecule (in mol L^{-1}) and P stands for the degree of polymerization, assuming that for $\alpha = 1$ each monomeric unit carries an elementary charge compensated by a monovalent counterion.

$$g = \Pi/\Pi_{id} = \Pi/RTC_p(P^{-1} + \alpha) \qquad (1)$$

Another osmotic coefficient g_p has been introduced by Katchalsky[1] starting from the assumption that it is particularly the contribution of the counterions that is much lower than the ideal one.

$$\Pi = RTC_p(P^{-1} + g_p\alpha) \qquad (2)$$

For sufficiently high molar masses the condition $g_p\alpha \gg P^{-1}$ will generally hold and $g \simeq g_p$. Osmotic coefficients can be determined directly with osmotic pressure measurements using semipermeable membranes. Information on the osmotic coefficient can also be obtained from elastic light scattering data. For a solution containing only one thermodynamic solute, the excess Rayleigh ratio of the solution over the solvent $\Delta R(\theta)$ for an angle θ is given by the equation

$$\Delta R(\theta) = \frac{K^*c\tilde{P}(\theta)RT}{(\partial\Pi/\partial c)}(1 + \cos^2\theta) \qquad (3)$$

Here, c is the concentration of macromolecules per unit volume, $\tilde{P}(\theta)$ is the intramolecular interference factor, which tends to unity for $\theta \to 0$, and K^* is given by

$$K^* = 2\pi^2\tilde{n}^2(\partial\tilde{n}/\partial c)^2(N_A\lambda^4)^{-1} \qquad (4)$$

with $\tilde{n}$ the refractive index of the solution and λ the wavelength of the incident light in vacuo. Combining (2) and (3) and expressing the concentration in mass per liter, one finds in the limit where $\tilde{P}(\theta) = 1$ the following expression:

$$\Delta R(\theta)^{-1} = (KM_mw)^{-1}\left\{P^{-1} + \alpha g_p + \frac{\partial(\alpha g_p)}{\partial \ln w}\right\} \qquad (5)$$

Here, M_m stands for the molar mass of monomeric unit, w is the concentration expressed in g L^{-1}, and K is identical with K^* except for the replacement of $(\partial\tilde{n}/\partial c)^2$ by $(\partial\tilde{n}/\partial w)^2$. The expression between the braces in (5) can be approximated by αg_p inasmuch as $P^{-1} \ll \alpha g_p$ and the concentration-dependence of αg_p is negligible in a good first approximation. Then $w/\Delta R(\theta)$ is proportional to αg_p. In the case of aqueous polyelectrolyte solutions very low values of $\Delta R(\theta)$ are found, which necessitates very precise measurements. These have been performed by Alexandrowicz[2] after painstaking purification of the solutions. Such precuations were found to be unnecessary with the equipment used here, and also because the intensities of scattered light by PAA solutions in methanol were larger than in water.

For ordinary polyelectrolyte solutions in water the reduced conductivity, defined by

$$\Lambda \equiv \kappa/(\alpha C_p \times 10^3) \qquad (6)$$

where κ is the conductivity (in Ω^{-1} m^{-1}) of the polyelectrolyte solution after correction for the conductivity of the solvent, has been found to increase with decreasing concentration at constant α,[3-5] to decrease with increasing degree of dissociation at constant C_p,[1,6] and to be independent of molar mass for $P > 200$.[7-12] Additionally, Λ increases with increasing ϵ,[13] just as is the case for low molar mass electrolytes. The reduced conductivity can be written as a sum of a contribution for the polyion and a contribution of the counterion. Usually this is put into the following form:

$$\Lambda = f(\tilde{\lambda}_p + \tilde{\lambda}_c°) \qquad (7)$$

Here, $\tilde{\lambda}_p$ represents the ionic conductivity of the polyion at the given concentration, $\lambda_c°$ is the ionic conductivity of the counterion at infinite dilution, and f is interpreted as the fraction of counterions contributing to the conductance of the solution (with conversely $1 - f$ the fraction of counterions assumed to shield the charge of the polyion by some kind of association). In order to determine f from conductance measurements, an independent assessment of $\tilde{\lambda}_p$ is needed. Transference measurements have been used for this purpose.[12,14-18] The values of f thus obtained appeared to be in satisfactory agreement with values derived for the fraction of "free" counterions from tracer diffusion measurements.[19]

II. Experimental Section

Poly(acrylic acid), its solutions, methanol, and the methoxides were as described in part 1. Concentrations of PAA and of methoxide were determined potentiometrically.

In the osmotic measurements a Knauer membrane osmometer was used with Satorius regenerated cellulose ultrafiltration membranes, resistant to methanol.

The osmometer was calibrated by appling a static pressure difference of 10 cm of methanol. In general, equilibrium pressure values were attained within 1–2 h. The measurements could give reproducible results within a few millimeters of methanol pressure. In the osmotic experiments, degrees of neutralization were limited to values where methanolysis was still negligible.

Scattering experiments were performed with a Chromatix KM6 low-angle He–Ne laser light scattering apparatus operating at 633 nm and room temperature. The intensity of the scattered light was measured at an angle of 5°, where $P(\theta) \simeq 1$. The Rayleigh factor of methanol at room temperature was determined to be $R_m = (2.88 \pm 0.15) \times 10^{-6}$ cm^{-1}. This value is in good agreement with the value measured by Kaye[20] at 23 °C, $R_m = (2.80 \pm 0.11) \times 10^{-6}$ cm^{-1}. For the scattering experiments the solutions were made dust-free by repeated filtration through Millipore FGLP filters (0.2 μm) immediately before measurement. Concentrations were determined spectrophotometrically after the scattering intensity measurements, using apparent extinction coefficients determined at four different wavenumbers as a function of α (see following paper, part 3 of the series). For the scattering measurements, solutions where methanolysis was not negligible were avoided. The scattering experiments gave results that were found to be reproducible within 10%.

A laser differential refractometer Chromatix KMX16, also operating at 633 nm, was used to determine the refractive index increment of the polyacrylate solutions. For $\tilde{n}$, appearing in the expression of K, the value of pure methanol at 20 °C and 633 nm,[21] $\tilde{n}_0 = 1.3274$, was used.

Conductances were measured with a Metrohm conductoscope E 365 in conjunction with a Philips dipping-type conductivity

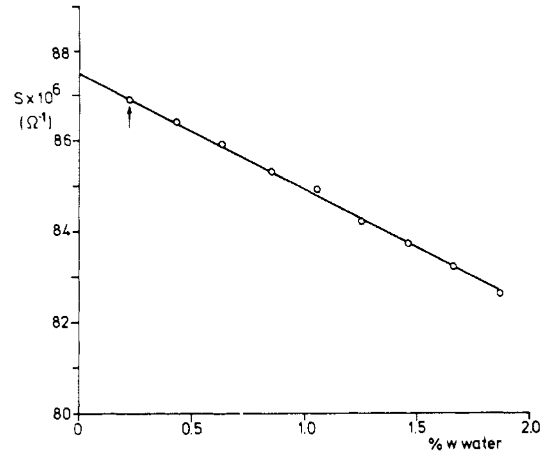

Figure 1. Conductance vs. weight fraction of water for PAA in methanol neutralized by CH_3OLi: $M = 5.3 \times 10^5$ g mol^{-1}, $C_p = 1.40 \times 10^2$ monomol L^{-1}. The arrow indicates the measuring point corresponding to the original solution.

cell sealed in the measuring vessel. The cell constant was 74 ± 1 m^{-1} as determined by calibration with aqueous KCl solutions. Solutions to be measured were continuously stirred and kept at constant temperature, 20.00 ± 0.05 °C, in the measuring vessel, which was permanently flushed with dry N_2 gas that had passed through gas wash bottles with H_2SO_4, NaOH pellets, and methanol, respectively. The methanol was replace if its specific conductivity became larger than 2×10^{-4} Ω^{-1} m^{-1}. Methoxide was added with a Radiometer ABU 11 autoburet, and conductance values were registered with a recorder. The measurements were performed in the following way. First a known amount of methanol was pipetted into the measuring vessel and flushed through with N_2. A constant conductance was reached, generally after approximately 1 h, with a value around 5×10^{-5} Ω^{-1} m^{-1}, which is slightly larger than that of methanol after exhaustive purification[22,24] but considered adequate for the measurements concerned. A small quantity of PAA stock solution was then pipetted into the vessel and the vessel was allowed to reach constant conductance. Finally, the buret outlet was brought in and the titration immediately started. The conductivity always very slowly increased with time ($(1\text{–}3) \times 10^{-5}$ Ω^{-1} m^{-1} h^{-1}). This effect was not fully understood and cannot be ascribed to evaporation only, as it was also observed with pure methanol. No correction for it was applied.

The specific conductance of the polyelectrolyte solutions was computed by the equation

$$\kappa = \frac{V_0 + v}{v_0}(S - S°)\tilde{Q} \tag{8}$$

Here, V_0 and v stand for the initial volume and the volume of the titrant added, respectively, S stands for the measured conductance of the solution, $S°$ stands for that of the pure solvent, and $\tilde{Q}$ is the cell constant. The error in Λ is estimated to be about 3%. Because of the slow increase with time of the conductance, values of κ for PAA neutralized with CH_3ONa at the higher α range could only be determined within 1×10^{-4} Ω^{-1} m^{-1}.

In order to find out whether small traces of water could have a large influence on the conductance of polyelectrolyte solutions in methanol,[25] water was added in small amounts to methanolic polyacrylate solutions and the subsequent change in conductance measured. This conductance was found to decrease linearly with increasing water content up to 2% (w/w) (see Figure 1). Such a lowering of conductance has been reported previously both for polyelectrolytes[26] and for low molar mass electrolytes[23,24,27] in methanol. If linear extrapolation to zero water concentration were permitted, it would show that the conductance of the solution as measured should not differ by more than 0.6% from that of a solution in absolute methanol. Therefore this error may be neglected in view of other errors.

When PAA in methanol was titrated with CH_3ONa, time effects were observed for higher values of α', which made a continuous titration unsuitable. After the addition of a certain quantity of titrant, the conductance did not reach a constant value immediately but changed over the course of time (see Figure 2). An analogous effect was also observed in the case of the potentiometric titration with CH_3ONa (see part 1). In Figure 2 the linear increases in conductance correspond to time intervals during which methoxide was continuously added. It can be seen that at low degrees of neutralization α' the apparent conductance S' remained constant after the addition was stopped. At higher values $\alpha' >$ 0.4, S' decreased after each addition of titrant. This decrease was more pronounced at higher values of α'. As is the case for the potentiometric titrations, no such time effects were observed when titrating PAA in water nor with CH_3Li in methanolic solutions.

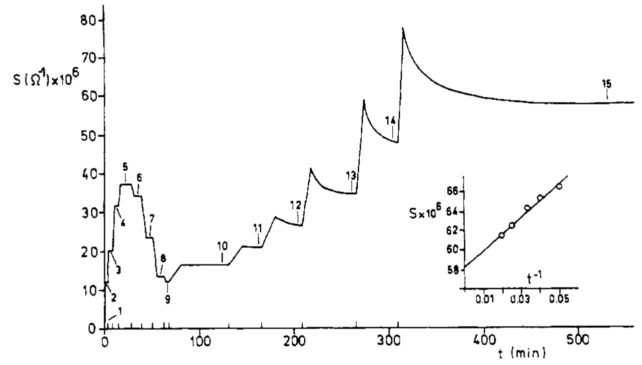

Figure 2. Discontinuous titration of PAA in methanol by CH_3ONa; $C_p = 1.19 \times 10^{-2}$ monomol L^{-1}. The additions of the methoxide are indicated on the abcissa. Numbers represent various degrees of neutralization α': (1) 0.00, (2) 0.01, (3) 0.03, (4) 0.05, (5) 0.08, (6) 0.12, 7) 0.17, (8) 0.22, (9) 0.25, (10) 0.38, (11) 0.51, (12) 0.64, (13) 0.75, (14) 0.84, (15) 0.91. Inset: conductance S' vs. reciprocal time t^{-1} for NaPPA/PAA, $\alpha' = 0.91$, in methanol (see text).

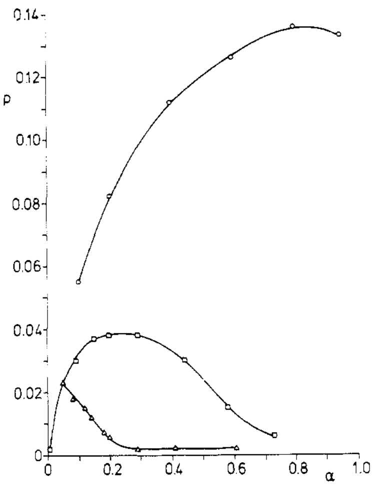

Figure 3. Change of αg_p with degree of dissociation for PAA in water neutralized by NaOH (○) (taken from ref 28), for PAA in methanol neutralized by CH_3ONa (△), and for PAA in methanol neutralized by CH_3OLi (□).

The correct values of S were obtained in the following way: after measuring S' for about 0.5 h, the conductance values of the tail of the curve were plotted against t^{-1} and extrapolated to $t \to \infty$ (see Figure 2, inset). It was checked several times that this extrapolated value agreed reasonably well with the measured conductance value after a sufficiently long time when S' becomes constant.

III. Results

The dependence of the osmotic coefficient g_p on the degree of dissociation was determined for two polymer concentrations as well as the dependence of g_p on the polymer concentration C_p at $\alpha = 0.20$ (the latter only for the case where Li^+ is the counterion). Values of αg_p and g_p were computed according to (2). Some of the results have been presented in Figures 3 and 4 and compared to

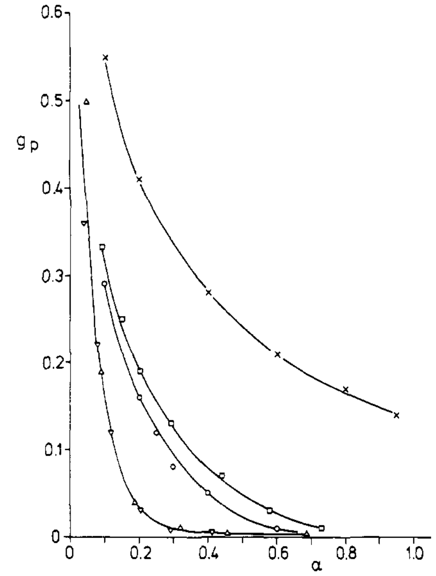

Figure 4. Osmotic coefficient g_p for various solutions of PAA: (×) PAA in water (C_p = 0.01 monomol L^{-1}) neutralized by NaOH (taken from ref 28); (□) PAA in methanol (C = 8.7 × 10^{-2} monomol L^{-1}) neutralized by CH_3OLi; (○) PAA in methanol (C_p = 1.70 × 10^{-2} monomol L^{-1}) neutralized by CH_3OLi; (△) PAA in methanol (C_p = 8.70 × 10^{-2} monomol L^{-1}) neutralized by CH_3ONa; (▽) PAA in methanol (C_p = 9.7 × 10^{-3} monomol L^{-1}) neutralized by CH_3ONa.

those of PAA in water.[28] As can be seen, g_p in methanol is generally much smaller than under corresponding conditions in water. In methanol for $\alpha > 0.1$, Na^+ ions are osmotically far less active than Li^+. With Na^+ the osmotic coefficient reaches already a very low value for $\alpha > 0.3$, which implies that under these conditions the counterions hardly contribute to the osmotic pressure. In the case of the titration in methanol with CH_3OLi, these low values are reached at much higher values of the degree of dissociation in the course of a continuous decrease of g_p.

From Figure 3 it can be seen that in the presence of Li^+ the values of αg_p for the methanolic solutions show a maximum with increasing α whereas in aqueous solutions only a constant value is reached at the higher end of the dissociation scale. The decrease of αg_p observed in methanolic solutions in the presence of Li^+ at higher α values is compatible with the results of viscosity measurements (see part 1). Figure 4 reveals that the α-dependence of the osmotic coefficient of PAA in methanol for $\alpha > 0.1$ is different in the presence of Na^+ from that in the presence of Li^+. For partially neutralized PAA in the presence of Na^+ there is no gradual decrease of g_p with increasing α, as observed in water but also for the methanolic system in the presence of Li^+. A rather more pronounced drop of g_p is observed to very low values in the same range of α values where the conformational transition was assumed to occur from the analysis of potentiometric and viscosimetric titrations with CH_3ONa of PAA in methanol.

In Figure 5 the variation of g_p with C_p for α = 0.20 in the presence of Li^+ as the counterion has been presented. The osmotic coefficient is seen to increase only slightly with increasing concentration.

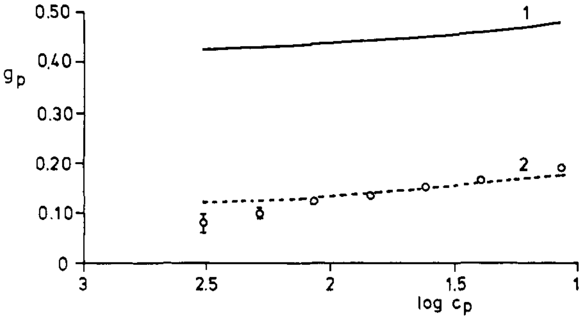

Figure 5. Concentration dependence of the osmotic coefficient g_p for LiPAA/PAA in methanol (α = 0.20): open circles represent the experimental points. The full drawn curve gives the theoretical variation of g_p according to the cell model for λ = 1.39 and a = 3.3 nm, and the dashed curve for λ = 6.0 and a = 0.7 nm (a is the radius of the cylinder representing the polyion).

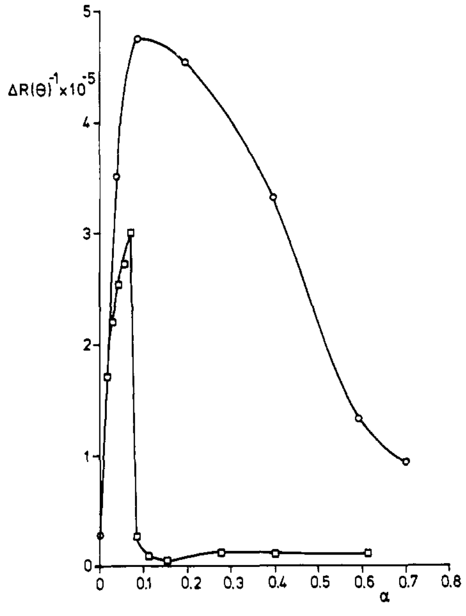

Figure 6. Reciprocal excess Rayleigh ratio $\Delta R(\theta)^{-1}$ vs. degree of dissociation α for PAA in methanol (2.9 g L^{-1}) neutralized by CH_3ONa (□) or by CH_3OLi (○).

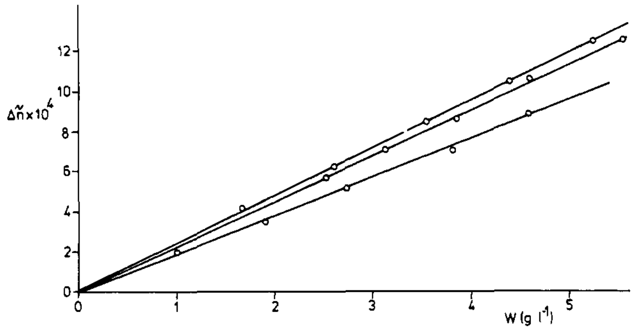

Figure 7. Refractive index increments $\Delta\tilde{n}$ vs. the concentration w (in g L^{-1}) for PAA in methanol neutralized with CH_3OLi to α = 0.40 (top line), α = 0.20, and α = 0.00 (bottom line).

Light scattering measurements were mostly performed with PAA solutions partially neutralized by CH_3OLi only. The reason can be seen in Figure 6, where the change in the reciprocal of the excess Rayleigh factor $\Delta R(\theta)$ with α has been presented for PAA in methanol at constant concentration and neutralized both by CH_3OLi and CH_3ONa. Although for low values of α the scattered intensity is nearly equal in both cases, at about α = 0.1 the scattering of methanolic PAA in the presence of Na^+ as counterion increases tremendously as compared to the situation in the presence of Li^+. Upon further increase $\Delta R(\theta)$ remains practically constant for the former whereas for the latter it first decreases and only then starts to increase again.

For PAA in methanol neutralized by CH_3OLi the specific refractive index increment was determined at seven different values of α (0.00 < α < 0.69) from the linear

Table I
Refractive Index Increment ($\partial\tilde{n}/\partial w$) Values for PAA in Methanol Neutralized by CH_3OLi

α	$(\partial\tilde{n}/\partial w)^a$	α	$(\partial\tilde{n}/\partial w)^a$
0.00	0.191	0.40	0.235
0.04	0.198	0.60	0.251
0.09	0.199	0.69	0.224
0.21	0.233		

^{a}The error in $(\partial\tilde{n}/\partial w)$ amounts to 0.005.

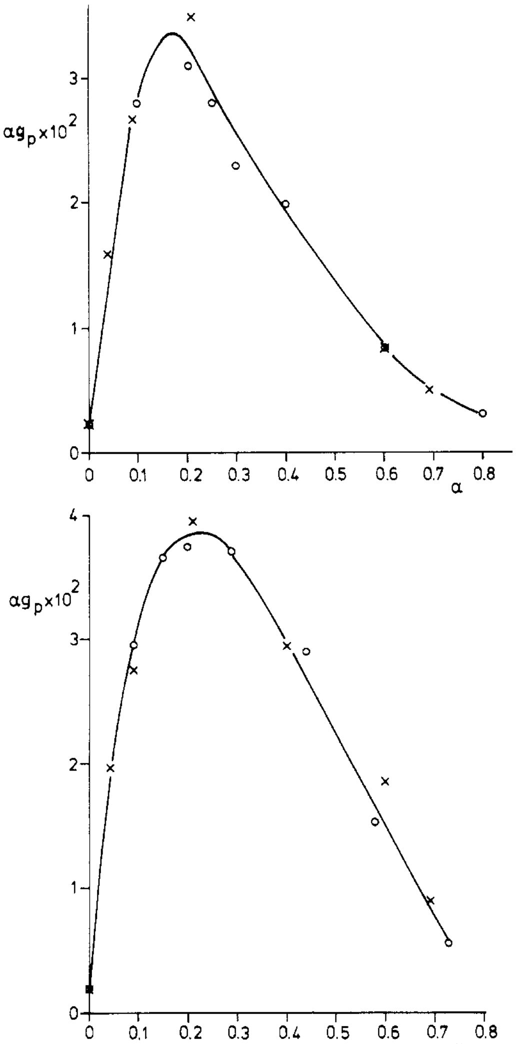

Figure 8. Change of αg_p with degree of dissociation for PAA in methanol neutralized by CH_3OLi: top, $C_p = 1.70 \times 10^{-2}$ monomol L^{-1}; bottom, $C_p = 8.70 \times 10^{-2}$ monomol L^{-1} [(×) osmotic pressure measurements; (○) light scattering measurements].

increase of $\Delta n \equiv \tilde{n} - \tilde{n}_0$ with concentration w (see, e.g., Figure 7). The values of $\partial\tilde{n}/\partial\tilde{w}$ have been collected in Table I; the estimated error is 0.005. With these specific increments the light scattering measurements can be used to evaluate αg_p according to (5) if the concentration dependence of this quantity is neglected. A surprisingly good agreement between the values of αg_p calculated in this way and values derived directly from osmotic measurements is found (Figure 8) at both concentrations investigated. This justifies a posteriori the assumption concerning the concentration dependence of αg_p. In the presence of Na^+ such a comparison is not possible except for the lowest values of α. Otherwise the scattered intensity is too high to allow an evaluation of αg_p according to (5). It should also be mentioned that in the presence of Na^+ opalescence has been observed at $\alpha > 0.1$ for higher concentrations than used in the present investigation. No precipitation of the macromolecule occurred however.

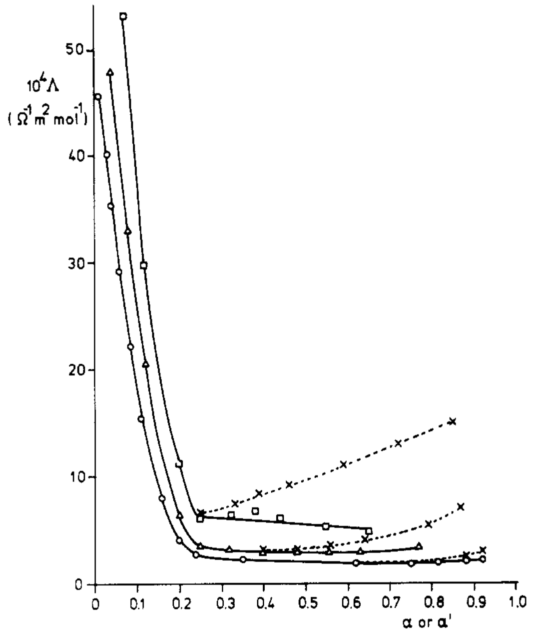

Figure 9. Reduced conductivity Λ vs. degree of dissociation α for PAA ($M = 5.3 \times 10^5$ g mol^{-1}) in methanol neutralized by CH_3ONa: (□) $C_p = 1.4 \times 10^{-3}$, (△) 6.48×10^{-3}, and (○) 2.85×10^{-2} monomol L^{-1}. The dashed curves (×) represent values without corrections for methanolysis; in that case the abscissa represents the degree of neutralization α'.

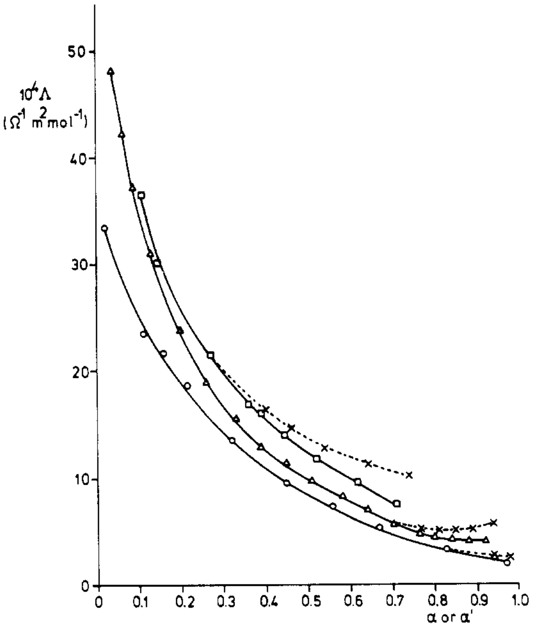

Figure 10. Reduced conductivity Λ vs. degree of dissociation α for PAA ($M = 5.3 \times 10^5$ g mol^{-1}) in methanol neutralized by CH_3OLi: (□) $C_p = 1.32 \times 10^{-3}$, (△) 6.47×10^{-3}, and (○) 2.75×10^{-2} monomol L^{-1}. For the significance of the dashed curves, see Figure 9.

In Figures 9 and 10 the reduced conductivity of PAA in methanol neutralized by CH_3ONa and by CH_3OLi respectively has been represented as function of α or α' for different macromolecular concentrations. Due to methanolysis the concentration of free methoxide ions may become nonnegligible, making a correction for the conductivity and also for the degree of dissociation necessary. Such a correction is possible by using the concentration of CH_3O^- at a given α' obtained from the potentiometric titrations and the value of the limiting ionic conductivity

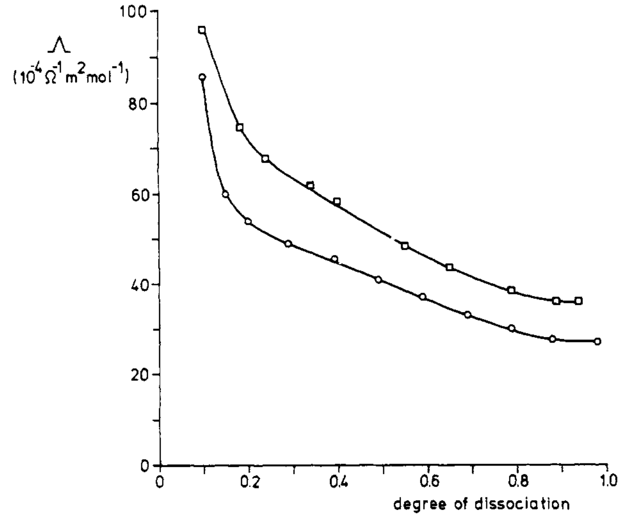

Figure 11. Reduced conductivity Λ of PAA in water ($M = 5.3 \times 10^5$ g mol^{-1}, $C_p = 1.80 \times 10^{-3}$ monomol L^{-1}) neutralized by NaOH (□) and LiOH (○).

Table II
Limiting Ionic Conductivity Values in Methanol at 20 °C Calculated according to (9)

ion	$\bar{\lambda}°_{293}$ (in Ω^{-1} m^2 mol^{-2}) × 10^4
Li$^+$	35.5
Na$^+$	41.2
CH_3O^-	47.8
H$^+$	129

of this ion in methanol at 20 °C (see Table II). Limiting ionic conductivity values at 20 °C have been computed from given values at 25 °C[22-24,27,29-32] using the relation

$$\bar{\lambda}°_T = \bar{\lambda}°_{298}\{1 + \zeta(T - 298)\} \qquad (9)$$

where $\lambda°_T$ represents the limiting ionic conductance at temperature T (K) and ζ the temperature coefficient, which has a value around 0.20 K^{-1}.[22,32] In Figures 9 and 10 the drawn curves represent the corrected values of Λ vs. α whereas the dashed parts refer to uncorrected values plotted against α' in the range where methanolysis has to be taken into account. For comparison, the values of Λ as a function of α for PAA in aqueous solutions at a single concentration also have been represented in Figure 11. Here the steeper decrease of Λ at low values of α can be ascribed to neutralization of H$^+$ ions arising from the self-dissociation of PAA in water, an effect that is practically absent in methanol (see part I).

For PAA in methanol the change of Λ with α is monotonous when it is titrated with CH_3OLi, in analogy to what is observed in water. Titration with CH_3ONa results in a different behavior of the reduced conductivity, the value of which drops rapidly to a very small value and remains practically constant for $\alpha > 0.25$. Such small values are attained at much larger values of the degree of dissociation in the case of the titration with CH_3OLi, e.g., for $\alpha > 0.6$. The concentration dependence of Λ at constant α is shown in Figure 12. A difference between the reduced conductivity in the presence of Na$^+$ and of Li$^+$ is only observed at higher α values, Λ in the presence of Na$^+$ being smaller than in the presence of Li$^+$ whereas $\bar{\lambda}°_{Na^+} > \bar{\lambda}°_{Li^+}$.

The dependence of Λ on the molar mass is also interesting. The change of Λ with α at constant concentration for four different molar masses in the range $5 \times 10^3 < M < 2 \times 10^6$ g mol^{-1} (corresponding to $75 < P < 30\,000$) is presented in Figures 13 and 14. Here two important observations can be made: (1) for the lower molar masses Λ depends on M but this dependence disappears at higher values of the degree of polymerization; (2) for the lowest values of M investigated the change of Λ with α is also montonous when PAA in methanol is titrated with CH_3ONa. Note for the sake of comparison that in aqueous polyelectrolyte solutions Λ has been found to be molar mass independent for $P > 200$ and to increase with decreasing M for $P < 200$.[5-8,10,12]

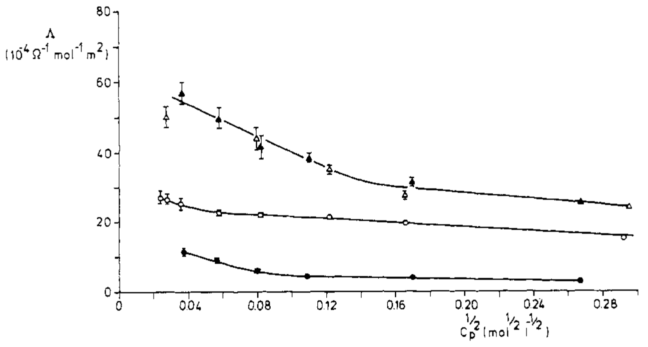

Figure 12. Concentration dependence of the reduced conductivity Λ for partially neutralized PAA in methanol: (△) LiPAA/PAA, $\alpha = 0.05$; (▲) NaPAA/PAA, $\alpha = 0.05$; (●) LiPAA/PAA, $\alpha = 0.20$; (○) NaPAA/PAA, $\alpha = 0.20$.

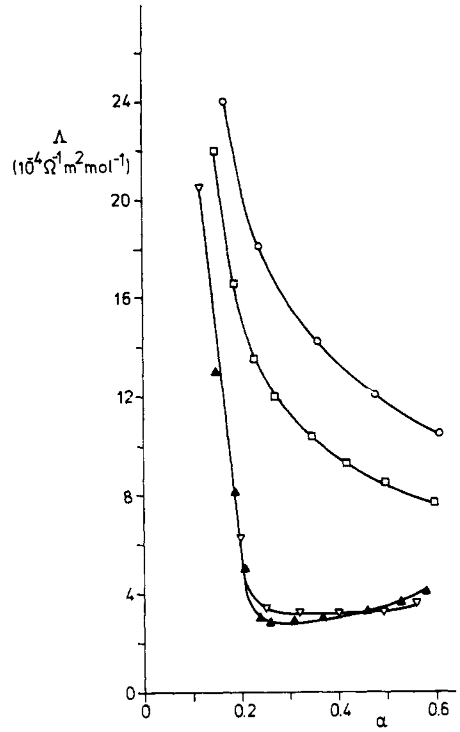

Figure 13. Reduced conductivity vs. degree of dissociation for PAA in methanol ($C_p \simeq 6.5 \times 10^{-3}$ monomol L^{-1}) neutralized by CH_3ONa. Results for various degrees of polymerization: (○) $P = 75$; (□) $P = 800$; (▽) $P = 7300$; (▲) $P = 30\,000$.

IV. Discussion

The results obtained with osmometry and conductance measurements confirm that PAA in methanol at room temperature and $\alpha > 0.1$ exhibits a qualitatively different behavior in the presence of Na$^+$ as a counterion from that in the presence of Li$^+$. In the latter case the variation of the osmotic coefficient and of the reduced conductivity with the degree of dissociation is monotonous, analogously to what is observed for PAA in water, whereas in the former there is a sharp decrease of these quantities to a very small value that from α around 0.25–0.30 on remains more or less constant. For the light scattering experiments

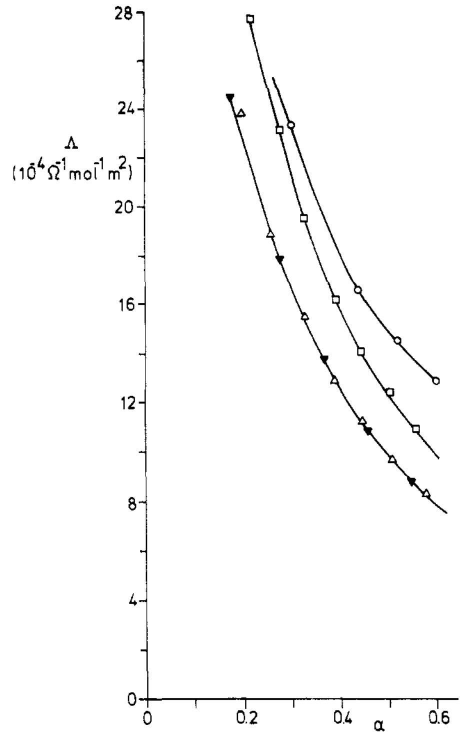

Figure 14. Reduced conductivity vs. degree of dissociation for PAA in methanol ($C_p \simeq 6.5 \times 10^{-3}$ monomol L^{-1}) neutralized by CH_3OLi. Results for various degrees of polymerization: symbols as in Figure 13.

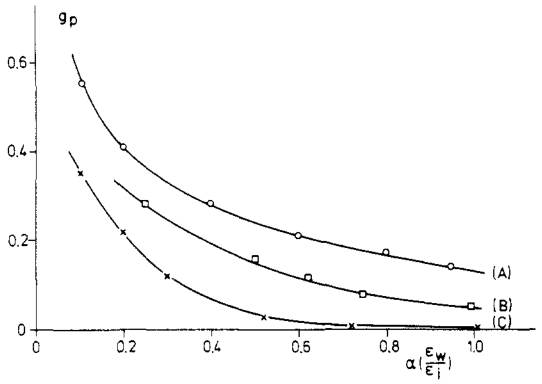

Figure 15. Change of the osmotic coefficient g_p with degree of dissociation corrected for the effect of relative permittivity ϵ_w/ϵ_i (see text). (A) NaPAA/PAA in water ($\epsilon_w/\epsilon_i = 1$); (B) LiPAA/PAA in methanol ($\epsilon_w/\epsilon_i = \epsilon_w/\epsilon_m$); (C) NaPAA/PAA in methanol ($\epsilon_w/\epsilon_i = \epsilon_w/\epsilon_m$). Here ϵ_w and ϵ_m represent the relative permittivity of water and methanol, respectively.

the intensity of the scattered light is much larger in the presence of Na^+ than in the presence of Li^+ in the same range of higher α values.

Two simple theoretical approaches have been used to interpret experimental values of the osmotic coefficient g_p. The first one, developed by Katchalsky and co-workers[1] uses a cylindrical cell model for which the Poisson–Boltzmann equation can be solved analytically in the case of a polyelectrolyte solution without low molar mass electrolyte. The value of g_p is given by the following equations.

$$g_p = (1 - \beta^2)/2 \qquad \lambda < \gamma/(1 + \gamma) \tag{10a}$$

$$g_p = (1 + |\beta|^2)/2\lambda \qquad \lambda > \gamma/(1 + \gamma) \tag{10b}$$

Here, λ is the charge parameter of the polyion, β an integration constant of the Poisson–Boltzmann equation, and γ a parameter related to the volume fraction y or concentration of the polyelectrolyte.

$$\gamma = -\ln (y^{1/2}) \tag{11}$$

The integration constant β is related to λ and γ through the relation

$$\lambda = \frac{1 - \beta^2}{1 + \beta \coth (\beta\gamma)} \tag{12}$$

which shows that for $\lambda < \gamma/(1 + \gamma)$ the value of $\beta^2 > 0$ whereas in the opposite case β^2 is negative. For the latter we then have $\beta^2 = -|\beta|^2$, $\beta = i|\beta|$, and $\beta \coth (\beta\gamma) = |\beta| \cot (|\beta|\gamma)$. In the case of an infinitely diluted solution ($\gamma = \infty$) this equation yields $\beta = 0$ for all $\lambda > 1$ and $\beta = 1 - \lambda$ for $\lambda < 1$. Equations 10a and 10b then reduce to

$$g_p = 1 - (\lambda/2) \qquad \lambda < 1 \tag{13a}$$

$$g_p = (2\lambda)^{-1} \qquad \lambda > 1 \tag{13b}$$

Equations 13a and 13b have also been derived by Manning from the line charge model at infinite solution for a polyelectrolyte in the presence of only monovalent small ions.[33] These equations have been tested more or less successfully for the case of aqueous polyelectrolyte solutions.[34-36]

It follows from (10) and (13) that at constant concentration (volume fraction) the osmotic coefficient is a unique function of λ. If the countour distance $A(\alpha = 1)$ between two successive charges on the chain for the fully charged macromolecule may be assumed to be the same in the two solvents, it follows that at a given concentration the charge parameter in methanol $\lambda^*(\alpha)$ is related to the charge parameter in water $\lambda(\alpha)$ by the simple equation

$$\lambda^*(\alpha) = (\epsilon_w/\epsilon_m)\lambda(\alpha) = (\epsilon_w/\epsilon_m)\lambda(\alpha = 1)\alpha \tag{14}$$

If the Poisson–Boltzmann cell model is valid and only electrostatic effects would be responsible for the change of g_p with α, the curve g_p vs. α in methanol should be superimposable on that of g_p vs. α in water if the scale on the x axis for the former is multiplied by ϵ_w/ϵ_m. Using values of g_p for PAA in water at 20 °C quoted by Katchalsky[28] from the work of Kern,[37] we have tried to compare them in this manner with the values at a comparable concentration in methanol with Li^+ as a counterion (Figure 15). The points do not fall on a single curve although the points in methanol lie on a curve more or less parallel with that in water. This confirms the conclusion also drawn in part I that although the results obtained with PAA in methanol in the presence of Li^+ look similar to those obtained in water, the difference cannot be ascribed to electrostatic effects only. In the case of PAA in methanol with Na^+ as counterions, there are additional deviations, which are most dramatically displayed in Figure 4, where also the differences with water are emphasized.

According to Katchalsky,[1,28] αg_p can be interpreted as an effective degree of disdociation, which in the case of water only increases slowly with increasing α. For PAA in methanol in the presence of Li^+ there is an initial increase followed by a broad maximum and a subsequent slow decrease whereas with Na^+ the initial increase stops already below $\alpha = 0.1$, followed by a rapid decrease to a very low value, which remains constant. The curve for PAA titrated in methanol with CH_3ONa is compatible with the suggestion that in the interval $0.10 < \alpha < 0.25$ a conformational transition occurs to a compact particle if it is assumed that most of the carboxylic groups, the carboxylate groups, and their corresponding counterions are inside the particle. This means that the net charge of the particle after the transition would be rather low and remain constant over the course of further titration.

This last assumption seems to be supported by the results of the conductometric titration with CH_3ONa, where it can be observed that the reduced conductivity above $\alpha = 0.25$ is small and practically constant. In terms of (7), one would expect the conformational transition to such a compact particle to be accompanied by a considerable reduction both in f and in λ_p, whereas both quantities would remain more or less constant after the transition. Titration in the range $\alpha > 0.25$ would affect the carboxylic groups, most of which would be in the inside of the compact particle, and would necessitate diffusion of both CH_3O^- and Na^+ ions into these particles. As this is in all probability a slow process, it could be responsible for the time effects observed during the conductometric titrations.

An interesting conclusion can be reached from the experiments in which the influence of the molar mass on the reduced conductivity was studied (see Figure 13 and 14). The dependence of Λ on α did not show the characteristic decrease below 25% dissociation observed for the higher molar masses in the case $P = 75$ and $P = 800$ when PAA is titrated with CH_3ONa. For these two low molar masses the conductometric titration in the presence of Na^+ resembles qualitatively that in the presence of Li^+ although quantitatively there are some differences that cannot be explained by the differences between $\tilde{\lambda}^\circ_{Na^+}$ and $\tilde{\lambda}^\circ_{Li^+}$. Apparently the transition to a compact particle cannot occur for macromolecules with a short chain length (note that for the two lowest degrees of polymerization the contour length is approximately 20 and 200 nm, respectively).

A more quantitative discussion of the conductivity values in the case of titration with CH_3OLi remains difficult as values for the ionic conductivity of the polyion $\tilde{\lambda}_p$ from independent measurements, e.g., transference measurements, are not available. According to (7), it is not possible to determine separately from conductance measurements only values for $\tilde{\lambda}_p$ and the fraction of counterions f contributing to the conductance of the solution. Of course, it remains possible to use for $\tilde{\lambda}_p$ the theoretical value derived by Manning[38] for polyelectrolytes with a charge parameter λ larger than unity.

$$\tilde{\lambda}_p = \frac{8.36 \times 10^4 J|\ln(\kappa_D a)||z|^{-1}}{1 + 1.30 \times 10^4 J|\ln(\kappa_D a)||z|^{-1}(\tilde{\lambda}^\circ_c)^{-1}} \qquad \lambda > 1 \qquad (15)$$

Here, κ_D^{-1} stands for the Debye–Hückel radius in which only screening by uncondensed counterions is considered such that

$$\kappa_D^{\,2} = 4\pi C_p N_A z^2 A(\alpha = 1) \times 10^3 \qquad \lambda > 1 \qquad (16)$$

and κ_D^{-1} is independent of the degree of dissociation. Further a is the polyion radius, z the counterion valency, and $\tilde{\lambda}^\circ_c$ the counterion limiting conductance. The constant J is defined by

$$J = 4q/3\eta Q \qquad (17)$$

where q is the elementary charge, $Q \equiv q^2/4\pi\epsilon\epsilon_0 kT$ the Bjerrum length, and η the viscosity of the solvent. Under the same condition $\lambda > 1$ the value of f according to Manning is given by

$$f = 0.886\lambda^{-1}|z|^{-1} \qquad \lambda > 1 \qquad (18)$$

It is generally found in aqueous solutions (see, e.g., ref 39) that the value of $\tilde{\lambda}_p$ according to (14) may differ considerably from the experimentally determined quantity although the theoretical equation predicts reasonably well the concentration dependence. On the other hand, according to the limiting law f should be a constant whereas it was found that f strongly depends on concentration.[39]

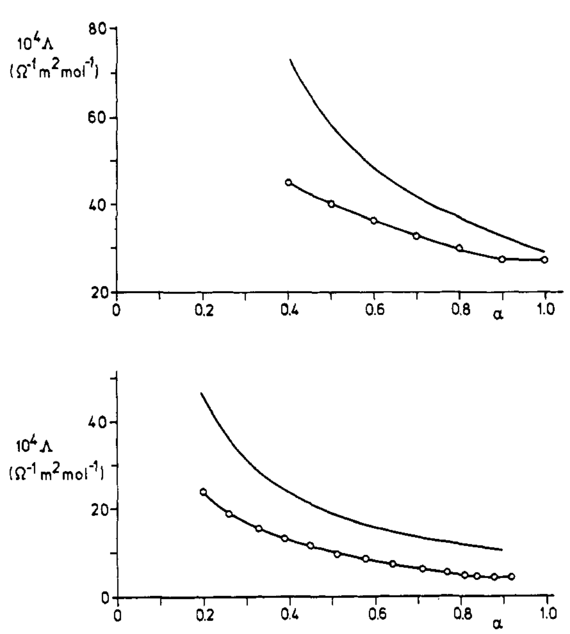

Figure 16. Comparison between experimental reduced conductivities (○) and theoretical predictions according to Manning (see text). Top, LiPAA/PAA in water, $C_p = 1.80 \times 10^{-3}$ monomol L^{-1}; $\eta = 1.00 \times 10^{-3}$ kg m^{-1} s^{-1}, $J = 2.39 \times 10^{-8}$ V^{-1} m^2 s^{-1}, $\tilde{\lambda}^\circ_{Li^+} = 35.2 \times 10^{-4}$ Ω^{-1} m^2 mol^{-1}, $\kappa_d^{-1} = 17.1$ nm, and $\tilde{\lambda}_p = 59.6 \times 10^{-4}$ Ω^{-1} mol^{-1} m^2 were used to calculate the theoretical values (full drawn curve). Bottom, LiPAA/PAA in methanol, $C_p = 6.47 \times 10^{-3}$ monomol L^{-1}; $\eta = 5.86 \times 10^{-4}$ kg m^{-1} s^{-1}, $J = 1.86 \times 10^{-8}$ V^{-1} m^2 s^{-1}, $\kappa_D^{-1} = 9.0$ nm, $\tilde{\lambda}_p = 39.3 \times 10^{-4}$ Ω^{-1} m^2 mol^{-1}, and $a = 0.3$ nm were used to calculate the theoretical values (full drawn curve).

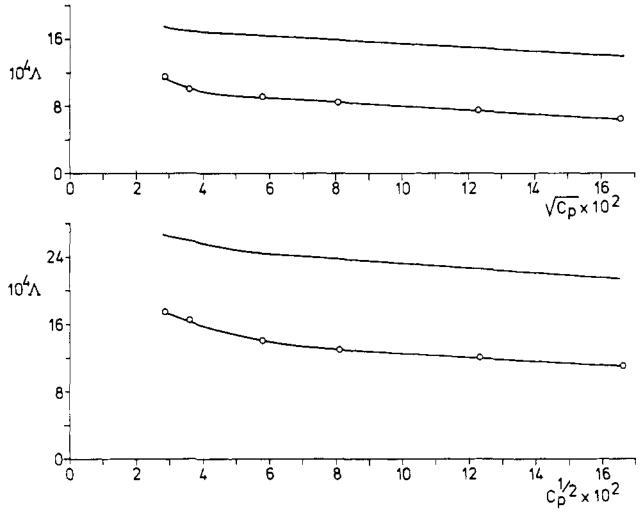

Figure 17. Concentration dependence of the reduced conductivity for LiPAA/PAA in methanol, $\alpha = 0.60$ (top) and $\alpha = 0.40$ (bottom): (—) theoretical curve according to Manning; (○) experimental results.

The same conclusions can be reached for PAA in methanol titrated with CH_3OLi at room temperature. Values of Λ as a function of α at constant C_p have been calculated according to (15) and (18) for those values of α for which the theoretical value of λ should be larger than unity in methanol ($\alpha > 0.15$). Also values of Λ as a function of C_p at two values of α have been calculated in the same way. In Figures 16 and 17 it is demonstrated that the theoretical values of Λ are in general larger than the experimental ones just as in the case of water. It follows from Manning's equations that the ratio Λ_m/Λ_w of the reduced conductance in methanol and that in water under comparable conditions should be independent of α for all cases where in both solvents $\lambda > 1$. Comparison of the experimental values of Λ for PAA in methanol and in water with

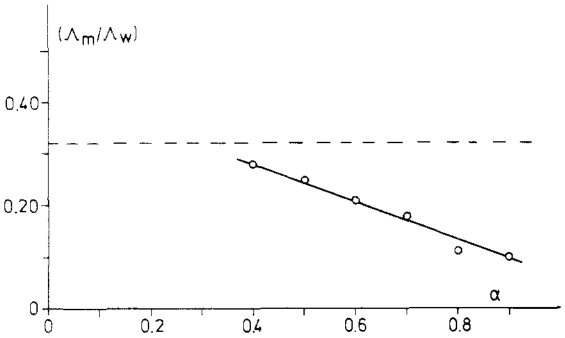

Figure 18. Ratio of the reduced conductivity in methanol (Λ_m) and reduced conductivity in water (Λ_w) vs. the degree of dissociation for LiPAA/PAA: dashed line, theoretical value according to (14) and (17); (○) experimental results as in Figure 16.

Li^+ as the counterion for $\alpha > 0.40$ at comparable concentrations (as Λ does not change appreciably with C_p for that range of degree of dissociation in both solvents) reveals however that Λ_m/Λ_w decreases by a factor 2 from $\alpha = 0.40$ to $\alpha = 0.90$ and remains below the theoretical value according to (14) and (17) (see Figure 18).

In conclusion it can be stated that in the qualitatively different behavior of PAA in methanol at room temperature in the presence of Na^+ as compared to Li^+ for $\alpha > 0.10$ has also been observed by osmotic pressure, elastic light scattering intensity, and conductivity measurements. The results obtained with these techniques are again compatible with the occurrence for $\alpha > 0.1$ of a conformational transition to a compact particle with a low net charge to which most of the counterions remain associated. This may explain the considerable reduction in the values of αg_p and Λ observed after this transition. The high intensity of the scattered light under these conditions (leading even to opalescence) could indicate that these compact particles are close to a phase transition although no precipitation was actually observed.

In the case where PAA in methanol was titrated by CH_3OLi no such conformational transition was revealed by the techniques explored. The differences between the experimental quantities in methanol and water cannot however be explained by classical polyelectrolyte theory taking only into account the difference in relative permittivity of both solvents. Possibly the formation of ion pairs at the higher α values, as postulated in part I, could be (partially) responsible for this. More information may be obtained from UV spectrophotometric results, which will be presented in part 3 of this series.

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Registry No. PAA, 9003-01-4; methanol, 67-56-1; lithium, 7439-93-2; sodium, 7440-23-5.

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