interpreted in both Θ and good solvent conditions. These molecular weight dependences of the thickness were in excellent agreement with the case of nonionic polymer adsorption.

However, the effect of NaCl concentration on the thickness of the adsorbed layer was different from that predicted by scaling concepts. The exponent of salt concentration dependence on the thickness was obtained to be around −0.2, and this absolute value was common among the available data. These coincident results, irrespective of polyion and experimental method, will be helpful in developing the theory.

The measured thickness t and $2\langle S^2\rangle^{1/2}$ are comparable, and this fact indicates that ellipsometry is sensitive to polymer segments at the periphery of the adsorbed layer.

Registry No. NaCl, 7647-14-5; platinum, 7440-06-4; (maleic acid)·(ethyl vinyl ether) (copolymer), 41315-86-0.

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Solvent Effects in Polyelectrolyte Solutions. 1. Potentiometric and Viscosimetric Titration of Poly(acrylic acid) in Methanol and Counterion Specificity

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ABSTRACT: Poly(acrylic acid) (PAA) in methanol at room temperature is shown to exhibit a conformational transition in the range $0.10 < \alpha < 0.25$ when neutralized with CH_3ONa. Viscosity measurements suggest that after this transition the polymer behaves as a small compact particle. Neutralization with CH_3OLi leads to a qualitatively different behavior without such a transition. This behavior is more analogous to that of PAA in water without added salt. However, neither the potentiometric nor the viscosimetric titration by CH_3OLi of PAA in methanol without added low molar mass electrolyte can be deduced from the results in water by the classical polyelectrolyte theory taking into account the change of the electric permittivity only.

I. Introduction

In polyelectrolyte theories electrostatic interactions are primarily assumed to determine the solution behavior. The solvent is considered as a continuum that influences these interactions only through its relative permittivity ϵ. Although this assumption seems to be quite reasonable in aqueous solutions and in agreement with experimental observations, the importance of nonelectrostatic interactions—particularly through specific solvent effects—cannot be ruled out altogether.[1]

In order to obtain a better understanding of the influence of the solvent on polyelectrolyte properties, an experimental study was undertaken on the behavior of a synthetic polyelectrolyte of very simple structure (poly(acrylic acid) (PAA)) in methanol. Methanol was chosen because it is in general a suitable solvent for electrolytes, and weak acids can easily be titrated in it. The physical and chemical properties of water and methanol do not differ too much[2,3] although the dielectric constant ϵ is only 31.4 in the latter at 25 °C as compared to 78.5 in the former. PAA was chosen for its very simple structure, the ease with which fractions of different molar mass can be prepared, and its good solubility in methanol. In aqueous solution it has been considered to behave as a typical weak polyacid without any complications.

We have investigated the solution behavior of PAA and partially ionized polyacrylates in methanol by several techniques. Ionization was performed by titration with a strong base, for which we have used lithium methoxide (CH_3OLi) and sodium methoxide (CH_3ONa). In the different parts of this series of papers the results obtained with the different techniques will clearly demonstrate that

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above a certain value of the degree of dissociation α the behavior of PAA in the presence of Li^+ differs from that in the presence of Na^+. In this paper potentiometric and viscosimetric titrations of PAA in methanol with both strong bases will be investigated.

The potentiometric titration of weak polyacids in aqueous solutions has been thoroughly studied. It was found that the *apparent pK* of the polyacid, defined by

$$pK \equiv pH + \log [(1 - \alpha)/\alpha] \qquad (1)$$

continuously increases with increasing α in the case of a typical polyelectrolyte such as PAA. This effect is ascribed to the increasing difficulty of dissociating an acidic group on the macromolecular chain with increasing charge on this chain.[4] More complicated titration curves have been observed with polyelectrolytes exhibiting a so-called *conformational transition*, such as, e.g., poly(glutamic acid) (PGA),[5] poly(methacrylic acid) (PMA),[6] and some copolymers of maleic acid.[7] For PGA the transition is interpreted as a change from a helical conformation to a more expanded one, and for the others as the change from a tightly coiled conformation to the expanded one. Such transitions can also be revealed by other techniques when those polyacids are titrated with a strong base. Much less is known about the potentiometric titration of polyelectrolytes in solvents other than water although such titrations can, in principle, be performed in the same way as in aqueous solutions or in water–solvent mixtures, e.g., with a conventional pH meter.

The contribution of macromolecules to the viscosity of their solution is generally expressed by the reduced viscosity η_{sp}/c (or a related quantity).

$$\eta_{sp}/c \equiv (\eta - \eta_0)/\eta_0 c$$

Here, η and η_0 stand for the viscosity of the solution and the solvent, respectively, with c representing the concentration of the solute. Extrapolation of the reduced viscosity to zero concentration yields the intrinsic viscosity $[\eta]$, which may give information about the average dimension of the macromolecule at infinite dilution. For solutions containing charged macromolecules without added low molar mass salt, the extrapolation of η_{sp}/c to $c = 0$ is impossible, although empirical methods have been proposed.[8] For these systems qualitative information can be obtained from the reduced viscosity at constant concentration. For instance the large increment of the reduced viscosity with increasing α at constant c observed for weak polyacids in water can be related to the uncoiling of the chains due to the increasing charge repulsions.

II. Materials and Methods

Atactic PAA was polymerized from acrylic acid by radical polymerization in the presence of H_2O_2 (30%) as used in this laboratory.[9] The heterogeneous material was fractionated by precipitation from ether/methanol solutions. The degree of polymerization P was determined viscosimetrically in 0.01 M aqueous HCl at 30 °C using the relation established by Newman et al.[10] Poly(acrylic acid) solutions were prepared by dissolving the polymer, after freeze-drying, in methanol. From IR, NMR, and potentiometric measurements no esterification of PAA in methanol could be detected.

Methanol was obtained from Merck or from Baker and was pa quality. It was used without further purification. No differences between the two products could be detected except that Baker's methanol showed a slightly smaller absorbance in the 200-nm region. The water content of the pa methanol was determined by a Karl Fischer titration; it was found to be 0.07% (w/w) (0.03 mol L^{-1}), somewhat higher than specified by the manufacturer (0.05%). In polyelectrolyte solutions the water content increases with PAA content as the freeze-dried PAA still remains between 0.25 and 1 molecule of water per monomer as could be determined from IR measurements. The influence of this nonnegligible amount of water on the physical behavior of PAA/methanol systems was checked by adding small but known quantities of water to the original solution and by subsequently measuring the corresponding change in the physical parameter observed. Then assuming that the different values could be extrapolated to zero water content, the extrapolated value could be compared to the value measured for the original solution. For practically all techniques used, and in particular for the potentiometric and viscosimetric titrations (see, e.g., Figure 1), the influence of the water content was found to be negligible.

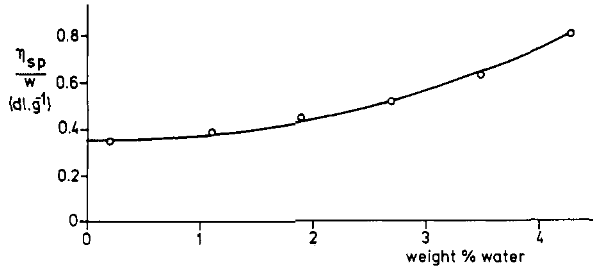

Figure 1. Change of the reduced viscosity of PAA ($M = 5.3 \times 10^5$ g mol^{-1}) neutralized to $\alpha' = 0.25$ in methanol by CH_3ONa with the weight fraction of water in the solution. The leftmost measuring point is that corresponding to the initial solution. The drawn line is the second-degree least-squares polynomial.

Methoxide solutions were prepared by stirring methanol for about 2 h in a three-necked flask with a reflux condenser, at room temperature and under a dry N_2 atmosphere, to minimize CO_2 and H_2O contamination and adding afterward sodium or lithium freshly cut from the pure metal. These cuttings had been washed in petroleum ether and petroleum ether/methanol before introducing them in the flask. The amount of alkali metal introduced was such that the final concentration of methoxide was approximately 0.3 M. Under these conditions the reaction was moderately fast. The reaction products were kept under a N_2 atmosphere and used as stock solutions.

Concentrations of PAA and methoxide were determined potentiometrically after diluting methanolic stock solutions with an excess of water.

LiBr and NaBr were purissimum from Merck or Baker. After drying at 200 °C in a vacuum drying oven for several days, the salts were dissolved directly in methanol. Glacial acetic acid was from Merck and was pa quality; dilute solutions were prepared by dissolving the glacial acid directly in methanol. These solutions were always freshly prepared in order to minimize esterification.[11] In our solutions the degree of esterification was found to be less than 0.5% from potentiometric and IR determinations.

All potentiometric titrations were performed with pH meters using a glass electrode (Radiometer G 202B) and a calomel electrode (Radiometer K 401). The pH of a methanolic solution (pH*) can according to Bates[12,13] be operationally defined the same way as in water. Calibration of the pH scale was performed with aqueous buffer solutions (Titrisol, Merck). The measured values pH′ of a methanolic solution are then related to pH* by the following relation.

$$pH' = pH^* - \log \gamma_H{}^t + \frac{E(m) - E(w)}{2.303(RT/F)} = pH^* + \delta \qquad (2)$$

Here, $E(i)$ represents the liquid junction potential of the cell in medium i (m = methanol and w = water) and $\gamma_H{}^t$ the formal transfer activity coefficient of the hydrogen ion from water to methanol (which determines the so-called medium effect). For univalent H^+, $\gamma_H{}^t = \exp(\Delta G^\circ{}_t/RT)$, where $\Delta G^\circ{}_t$ stands for the formal Gibbs energy change when 1 mol of H^+ is transferred from its standard state in water to its standard state in methanol. The value $\delta = -2.34$ for methanol/water was taken from the literature.[12,14] This value is reliable as the liquid junction potential of the cell has been found to be reasonably constant and independent of the type of calibrating buffer used.[14,15] Furthermore, glass electrodes give stable readings in methanol after being conditioned in this solvent.[11,16,17] The electrodes were always kept in pure methanol overnight before a titration was started. At the

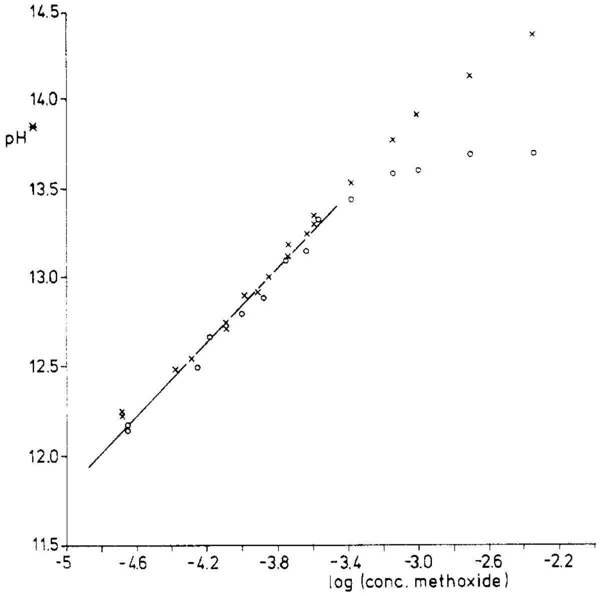

Figure 2. Alkaline error of the glass electrode in methanol for CH_3ONa (○) and CH_3OLi (×) solutions (see text).

end of the measuring day the electrodes were checked again against the aqueous buffers; within 10 min stable readings were observed that corresponded to the original calibration.

Titrations with CH_3OLi were performed with Radiometer automatic titration equipment consisting of a TTT-11 Titrator in conjunction with an SBR 2c Titrigraph and a pH meter 26. Because titrations with CH_3ONa showed time effects in the pH at the higher degrees of neutralization when the titration was stopped, a discontinuous titration method was used in that case. Titrant was added though a Radiometer ABU 11 autoburet and the pH meter 26 was coupled to a recorder. After addition of an aliquot of titrant, pH′ was allowed to stabilize before the titration was continued. All titrations were carried out in a vessel thermostated at 25.0 ± 0.1 °C and under a dry N_2 atmosphere. Duplication of the titration curves was possible to within 0.1 pH′ unit except at the very beginning of the titration curve, where the slope of pH′ vs. α' is large (α' is the degree of neutralization).

At the higher pH′ end of the titration, corrections for the alkaline error of the glass electrode have to be applied. In Figure 2 the experimentally determined pH* values have been plotted as a function of the logarithm of the methoxide concentration. It can be seen that differences between the measurements in the presence of Li^+ and Na^+ appear for $C_{CH_3O^-} > 3 \times 10^{-4}$ mol L^{-1} and that the alkaline error is larger for Na^+ than for Li^+. From these measurements the autoprotolysis constant K_{meth} of methanol can also be calculated if activity coefficient corrections are neglected. For $C_{CH_3O^-} = 10^{-4}$ M, a pH* 12.8 is found; thus $K_{meth} = 16.8$ is in good agreement with the value 16.7 quoted in the literature.[18] This agreement justifies additionally the value of δ that has been used.

The values of η_{sp} were calculated directly from the flow times of the solutions and of the solvent (which could be either pure methanol or methanolic salt solutions) determined with the help of Schott (Type KPG) Ubbelohde viscosimeters with an automatic Schott AVS measuring system. No corrections for the change in density from solvent to solution were applied. All measurements were performed at 25.00 ± 0.05 °C. All viscosity experiments were performed in a glovebox flushed with CO_2-free N_2, as carbon dioxide appeared to have a drastic decreasing effect on the flow time of the solutions. All samples were also prepared in the same box by adding known aliquots of methoxide to stock solutions of PAA. Dilution was performed by adding methanol to solutions. With the precautions mentioned, flow times could be measured with an accuracy up to 1%. Without them, time effects were noticed for LiPAA at higher degrees of neutralization only.

Two viscosimeters with different capillary diameters were used with flow times for pure methanol of about 75 and 240 s, respectively, and apparent shear gradients of 800 and 1100 s^{-1}. All solutions gave the same value of η_{sp} with both viscosimeters. Therefore it can be concluded that shear effects do not have to be taken into account as expected because non-Newtonian behavior is generally found for higher molar masses and much higher solution viscosities.[9,10]

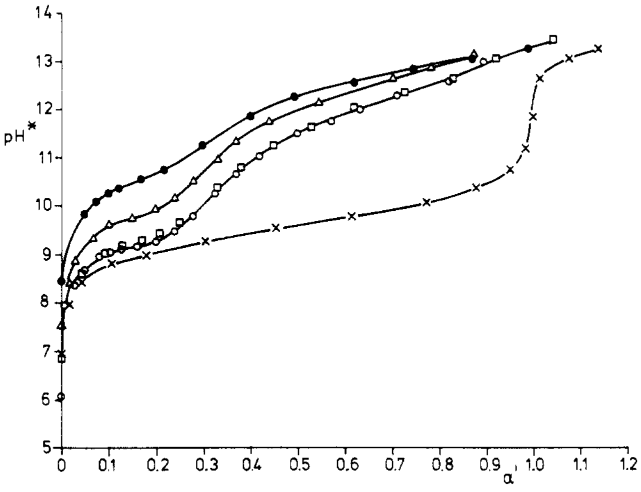

Figure 3. Titration curve of PAA ($M = 5.3 \times 10^5$ g mol^{-1}) in methanol by CH_3ONa; no added salt. Concentrations: 3.22×10^{-3} (●); 8.83×10^{-3} (△); 1.93×10^{-2} (□); 6.77×10^{-2} (○) monomol L^{-1}. For comparison, the titration curve of acetic acid (×) 2.08×10^{-2} M in methanol is also presented.

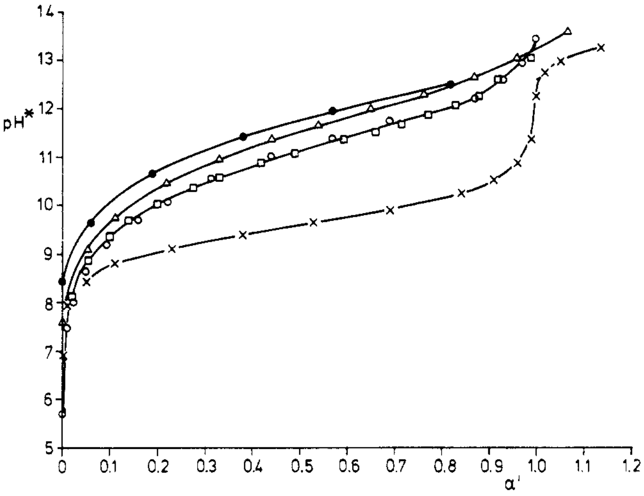

Figure 4. Titration curve of PAA ($M = 5.3 \times 10^5$ g mol^{-1}) in methanol by CH_3OLi; no added salt. Concentrations: 2.24×10^{-3} (●); 6.14×10^{-3} (△); 1.93×10^{-2} (□); 4.71×10^{-2} (○) monomol L^{-1}. For comparison, the titration curve of acetic acid (×) 2.08×10^{-2} M in methanol is also presented.

III. Results

In Figures 3 and 4 typical potentiometric titration curves of PAA with CH_3ONa and CH_3OLi are shown for different concentrations of polyelectrolyte but in the absence of low molar mass electrolyte. The degree of neutralization is defined as usual.

$$\alpha' = C_B/C_p \tag{3}$$

Here, C_B is the concentration of added base and C_p is the monomolar polyelectrolyte concentration (both in molarity). It is obvious that in methanol the titration curve of PAA in the presence of Na^+ as counterion is different from that in the presence of Li^+. This is not observed for the titration of acetic acid in methanol, which gives the usual curve of a normal weak acid in both cases. The titration of PAA in the presence of Li^+ exhibits a monotonous rise of pH* with α' without any buffering effect. This corre-

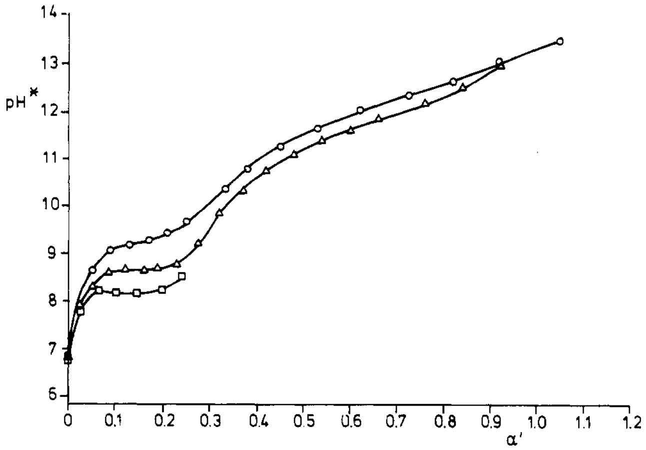

Figure 5. Titration curve of PAA ($M = 5.3 \times 10^5$ g mol^{-1}) in methanol ($C_p = 1.93 \times 10^{-2}$ monomol L^{-1}) by CH_3ONa at various NaBr concentrations. C_s: 0 (○); 1.32×10^{-3} (△); 4.34×10^{-3} (□) M. At the highest salt concentration, precipitation occurred for $\alpha' > 0.24$.

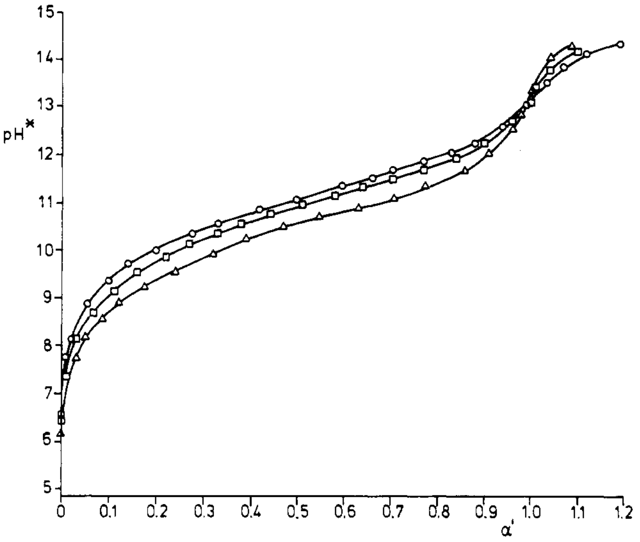

Figure 6. Titration curve for PAA ($M = 5.3 \times 10^5$ g mol^{-1}) in methanol ($C_p = 1.93 \times 10^{-2}$ monomol L^{-1}) by CH_3OLi at various LiBr concentrations. C_s: 0 (○); 1.31×10^{-3} (□); 8.43×10^{-3} (△) M.

sponds to what is found in the titration of PAA in water irrespective of the alkaline counterion present. In contrast, the titration of PAA in methanol with CH_3ONa shows that in the region $0.10 < \alpha' < 0.25$ the change of pH* with α' is considerably reduced. This flattening in the curve of pH* vs. α' becomes more pronounced with higher polyelectrolyte concentration.

When bromide is added the titration curves in the presence of Na$^+$ as counterion remain different from those in the presence of Li$^+$ (see Figures 5 and 6). In the former case, not only is the usual lowering of pH* with increasing salt concentration C_s observed, but flattening of the curve appears at a lower α' value. Higher concentrations of salt were not investigated because with NaBr, salting out occurred for $C_s = 4.34 \times 10^{-3}$ M at $\alpha' > 0.24$. Note that in the presence of Li$^+$, no salting out was observed for a value of C_s twice as large up to $\alpha' = 1$, however.

From the titration curves the degree of dissociation α defined by

$$\alpha = \alpha' + (C_{H^+} - C_{CH_3O^-})/C_p \qquad (4)$$

can be calculated if activity coefficients can be put equal to unity, i.e., if it may be assumed that $C_{H^+} \simeq 10^{-pH^*}$ and $C_{CH_3O^-} \simeq K_{Meth}/C_{H^+}$. It thus is found that at low α' the self-dissociation of PAA is negligible in methanol (e.g., at $C_p = 1.5 \times 10^{-2}$ monomol L^{-1} and $\alpha' = 0$ we find $\alpha = (5 \pm 2) \times 10^{-6}$ whereas in water under the same conditions, $\alpha = (3.0 \pm 0.3) \times 10^{-2}$). Methanolysis however starts to be significant around pH* 12.5 or higher, a pH* that is reached at lower values of α' in the presence of Na$^+$ than of Li$^+$ (see Figures 3 and 4). In the case of aqueous PAA solutions, hydrolysis effects can generally be neglected whereas self-dissociation may be important, especially at low polyelectrolyte concentrations. Thus PAA is a weaker acid in methanol than in water.

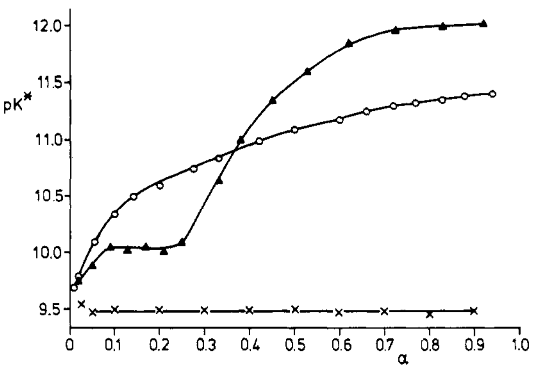

Figure 7. Change of pK* with α for PAA in methanol ($C_p = 1.43 \times 10^{-2}$ monomol L^{-1}) titrated with CH_3ONa (▲) and CH_3OLi (○) in the absence of added salt. For comparison, the analogous variation for acetic acid in methanol (2×10^{-2} M) is also presented (×).

Another way of representing potentiometric titration curves is to plot the apparent pK*, as defined by (1), against α. An example of such a plot is given in Figure 7, but the features remain the same under different conditions. In contrast to the constant value of pK* for acetic acid, for PAA the pK* tends to increase with increasing α. The difference between the titration behavior of PAA in the presence of Li$^+$ and of Na$^+$ as counterion is emphasized by this representation. Only for the latter a region of nearly constant pK* is observed for $0.10 < \alpha < 0.25$. This plateau is followed by a steep rise of the pK* above the values found for the titration in the presence of Li$^+$. In the beginning of the titration the difference between the two curves is small however. At the end of the titration the two curves become more or less parallel but then there is hardly an increase in pK* anymore, indicating that for $\alpha > 0.6$, the charge effects are strongly reduced.

A third representation for potentiometric titrations is the so-called Henderson–Hasselbalch plot, in which in general pH is represented as a function of log $[(1 - \alpha)/\alpha]$. As first observed by Katchalsky and Spitnik[20] many polyacids give over a more or less wide range around $\alpha = 0.5$ a straight line with a slope n larger than unity

$$\mathrm{pH} = \mathrm{p}K_a - n \log [(1 - \alpha)/\alpha] \qquad (5)$$

with $\mathrm{p}K_a = (\mathrm{pH})_{\alpha=0.5}$. Both n and pK_a depend on C_p and C_s. Henderson–Hasselbalch plots for PAA in methanol are presented in Figure 8. In the presence of Li$^+$ the variation of pH* with log $[(1 - \alpha)/\alpha]$ is linear over a broad range of the degree of dissociation. In the presence of Na$^+$ the plot is much more complicated, exhibiting two linear regions for $\alpha < 0.6$ with different n^* separated by a transition region around $0.10 < \alpha < 0.25$ (see Table I). The same kind of Henderson–Hasselbalch plot has been obtained with PMA in water.[6]

Viscosimetric titrations also reveal characteristic differences between solutions with Li$^+$ or Na$^+$ as counterions. In Figure 9 the α' dependence of the reduced viscosity

Table I
Potentiometric Titration Parameters from Least-Squares Fits for PAA ($M = 5.3 \times 10^5$ g mol^{-1}) in Methanol ($C_p = 1.93 \times 10^{-2}$ monomol L^{-1}) and in Water ($C_p = 1.50 \times 10^{-2}$ monomol L^{-1})

solvent	titrant	salt added	C_s	$(pK_a)_1{}^a$	$n_1{}^a$	$(pK_a)_2{}^b$	$n_2{}^b$	pK_0	S_y
water	NaOH			6.32	2.12			4.73	0.05
	NaOH	NaBr	8.05×10^{-3}	5.99	2.09			4.14	0.02
methanol	CH_3OLi			11.05	1.75			9.7	0.06
	CH_3OLi	LiBr	1.30×10^{-3}	10.90	1.85			9.4	0.04
	CH_3OLi	LiBr	8.40×10^{-3}	10.50	1.80			9.0	0.04
methanol	CH_3ONa			10.9	1.8	11.5	3.9		
	CH_3ONa	LiBr	1.30×10^{-3}	10.0	1.3	11.4	5.0		

[a] For titration in methanol and in the presence of Na^+ these parameters correspond to the region $\alpha \le 0.1$; for all other cases they correspond to the region $0.02 \le \alpha \le 0.7$. [b] The parameters in methanol and in the presence of Na^+ correspond to the region $0.25 \le \alpha \le 0.6$.

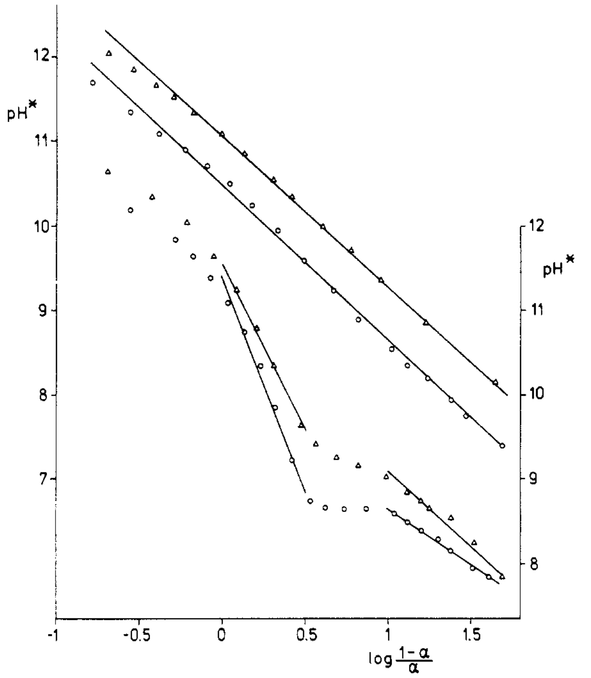

Figure 8. Henderson–Hasselbalch plots for the titration of PAA in methanol by CH_3OLi (upper straight lines and ordinate on the left) and by CH_3ONa (two lower curves and ordinate on the right) for $C_p = 1.93 \times 10^{-2}$ monomol L^{-1}. LiPAA/PAA: no salt (△) and 8.43×10^{-3} M LiBr (○). NaPAA/PAA: no salt (△) and 1.32×10^{-3} M NaBr (○).

(expressed as η_{sp}/w, with w the concentration in g dL^{-1}) is presented for a sample of PAA at three different concentrations in methanol and neutralized by CH_3OLi. The curves are qualitatively somewhat reminiscent of the analogous ones for PAA in water neutralized with NaOH albeit the absolute values of η_{sp}/w for the latter are generally larger, the maximum is situated around $\alpha' = 0.5$, and the decrease of the reduced viscosity at higher degrees of neutralization is less pronounced (near $\alpha' = 1$ the value of η_{sp}/w is about 80% of the value at the maximum).[21,22] The reduced viscosity of PAA in methanol–Li^+ solutions is very sensitive to an increase of the ionic strength of the solution, as demonstrated in Figure 10.

More surprising is the behavior of PAA with Na^+ as counterion as revealed by the plots of η_{sp}/w vs. α' (see Figure 11). Here, after an initial rise as observed in the presence of Li^+, the reduced viscosity decreases drastically in a small interval around $\alpha' = 0.15$. Very low values of η_{sp}/w are found for $\alpha' > 0.25$ irrespective of C_p. In fact these values are much *lower* than the reduced viscosities of unneutralized PAA in methanol and independent of α' within experimental accuracy. They also seem to be hardly affected by the presence of low molar mass electrolyte (see Figure 12). The polyelectrolyte concentration is of little

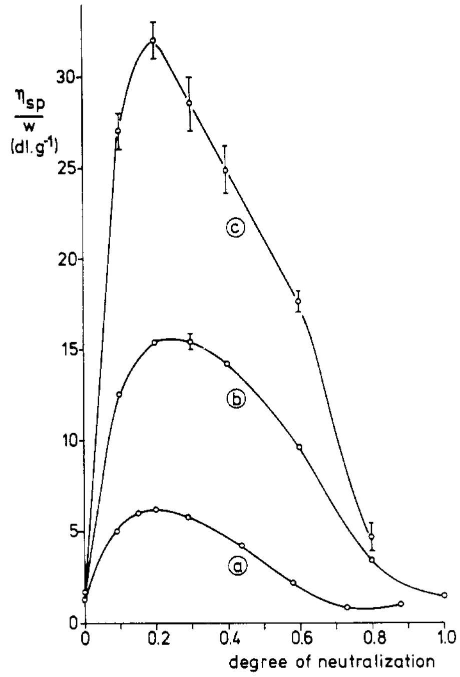

Figure 9. Reduced viscosity as a function of degree of neutralization for PAA ($M = 5.5 \times 10^5$ g mol^{-1}) in methanol neutralized by CH_3OLi; no salt added. Polyelectrolyte concentrations: 8.7×10^{-2} (a), 1.7×10^{-2} (b), and 3.4×10^{-3} (c) monomol L^{-1}.

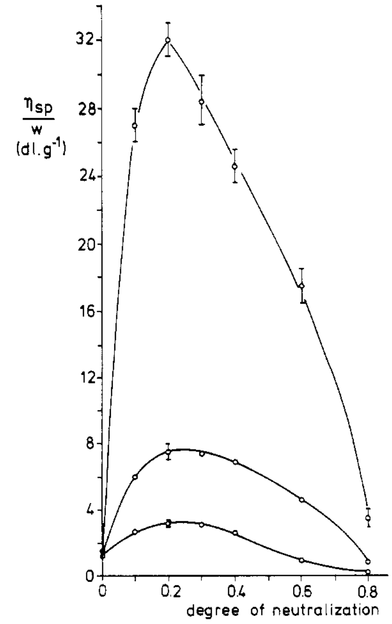

Figure 10. Influence of LiBr on the reduced viscosity of Li-PAA/PAA in methanol (same sample as in Figure 9, $C_p = 3.4 \times 10^{-3}$ monomol L^{-1}). Salt concentrations from top downwards: 0, 1×10^{-3}, and 5×10^{-3} M.

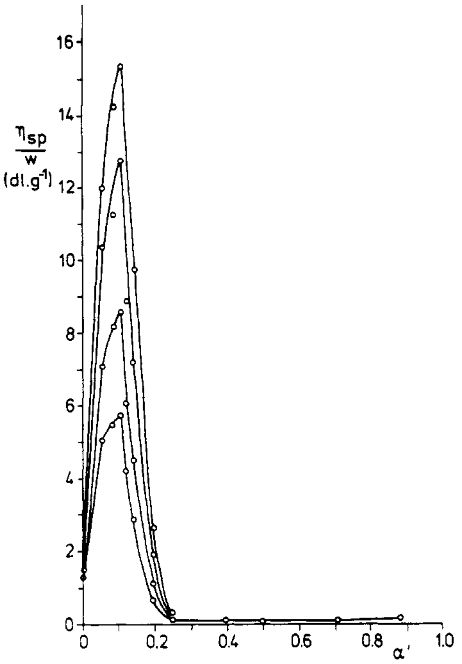

Figure 11. Reduced viscosity as a function of degree of neutralization α' for PAA (M = 5.5 × 10^5 g mol^{-1}) in methanol neutralized by CH_3ONa; no salt added. Polyelectrolyte concentrations from top downward: 2.9 × 10^{-3}, 5.8 × 10^{-3}, 1.2 × 10^{-2}, and 2.3 × 10^{-2} monomol L^{-1}.

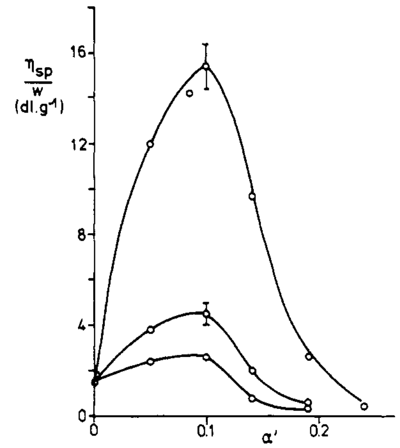

Figure 12. Influence of NaBr on the reduced viscosity of NaPAA/PAA in methanol (same sample as in Figure 11). Curves from top downward: C_p = 2.9 × 10^{-3} monomol L^{-1}, C_s = 0; C_p = 2.8 × 10^{-3} monomol L^{-1}, C_s = 3.3 × 10^{-4} M; C_p = 2.6 × 10^{-3} monomol L^{-1}, C_s = 9.2 × 10^{-4} M.

influence on the position of the maximum of η_{sp}/w vs. α'.

The molar mass dependence of the viscosity of NaPAA in methanol for α' > 0.25 is also surprising. Reduced viscosities as a function of w for five different molar masses 7.5 × 10^4 < $\bar{M}$ < 2.25 × 10^6 g mol^{-1} at α' = 0.30 are presented in Figure 13. For comparison, measured values of η_{sp}/w for unneutralized PAA in aqueous 0.01 M HCl at 30 °C (solutions close to Θ-conditions[9]) are also shown in the same figure. These results demonstrate that the absolute values of η_{sp}/w for neutralized PAA in methanol at α' = 0.30 are much smaller than for unneutralized PAA in a Θ-solvent and have a less pronounced molar mass dependence (in aqueous 0.01 M HCl the extrapolated values $[\eta]$ are linearly dependent on $M^{1/2}$). At the higher values of $\bar{M}$ ($\bar{M}_\eta \geq$ 5.5 × 10^5 g mol^{-1}) even no significant change of η_{sp}/w with M is observed. Finally there seems to be a definite *increase* of the reduced viscosity with decreasing concentration. Such an increase is usually observed with charged polyelectrolytes in the absence of low molar mass electrolyte but here the total amplitude of the effect is rather small and is probably due to a small increase of the degree of dissociation with decreasing w.

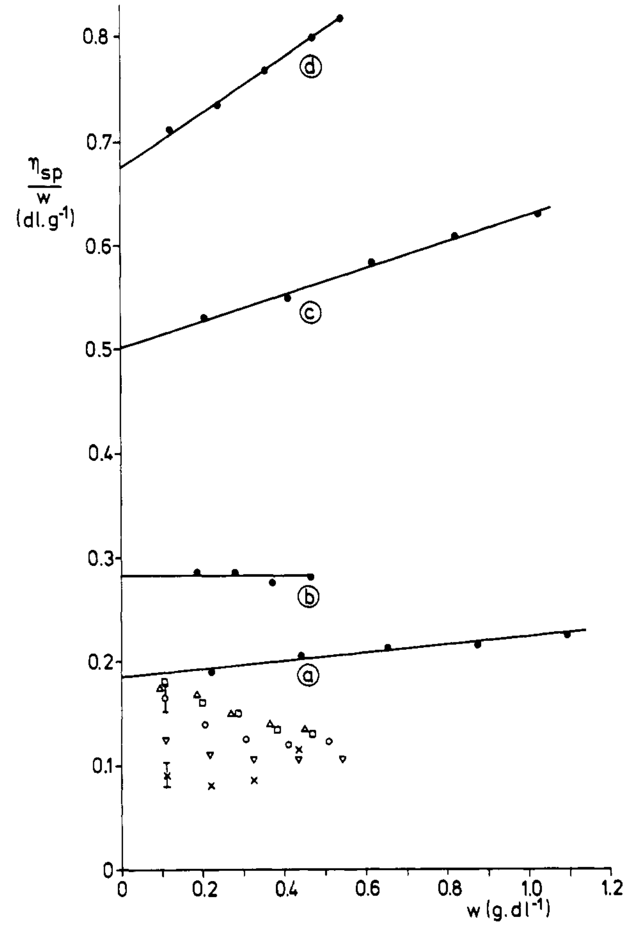

Figure 13. Reduced viscosity vs. polyelectrolyte concentration for PAA in 0.01 M aqueous HCl at 30 °C and for NaPAA/PAA, α' = 0.30 in salt-free methanol. The influence of the molar mass is shown by results with M = 7.5 × 10^4 ((●) and line b in water; (×) in methanol), 5.5 × 10^5 ((●) and line c in water; (○) in methanol), 9.9 × 10^5 ((●) and line d in water; (□) in methanol), and 2.25 × 10^6 g mol^{-1} ((△) in methanol).

An interesting observation is that the influence of the counterion on the viscosity of PAA in methanol is independent of the way in which the counterion is introduced into the solution, i.e., either via the polyacrylate or via the low molar mass electrolyte. The counterion present in excess determines the overall solution viscosity (see Figure 14). When both Li^+ and Na^+ counterions are present in equal amounts, i.e., for α' = C_s/C_p in the mixed case, the viscosities of NaPAA/LiBr and of LiPAA/NaBr are equal. A specificity of the counterions at α' = 0.04 is also observed but the effect is small. Such a specificity has already been found in aqueous solutions of polyelectrolytes but at much higher salt concentrations.[23,24] In these cases Na salts were found to have a larger depressing effect on the solution viscosity than Li salts.

IV. Discussion

In methanol a difference exists between the titration behavior of PAA in the presence of Li^+ or of Na^+ as counterions. Qualitatively, the titration curves with Li^+ resemble those of PAA in water in the presence of monovalent alkaline counterions although some important differences will be discussed below. The potentiometric titration of PAA with CH_3ONa is analogous to that of a polyelectrolyte in water undergoing a conformational transition with increasing degree of dissociation. Before

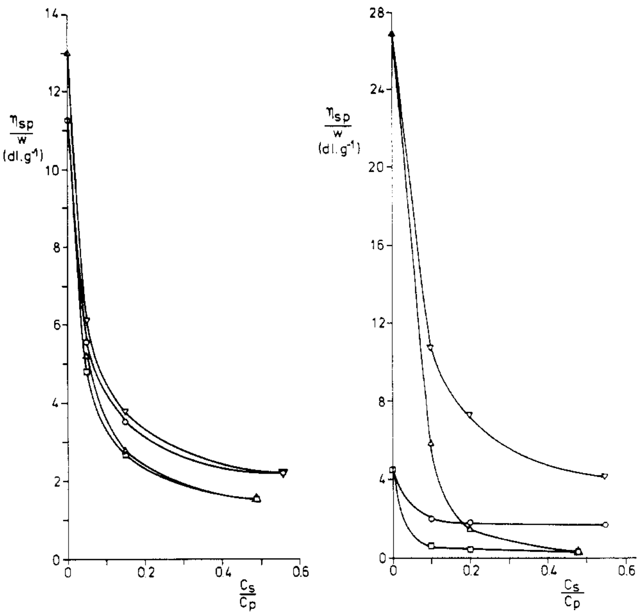

Figure 14. Reduced viscosity of polyacrylate/poly(acrylic acid) mixtures in methanol as a function of the ratio C_s/C_p (PAA: $M = 5.5 \times 10^5$ g mol^{-1}, $C_p = 5.0 \times 10^{-3}$ monomol L^{-1}). Left, curves for $\alpha' = 0.04$; right, curve for $\alpha' = 0.18$. Systems: LiPAA/PAA + LiBr (▽), LiPAA/PAA + NaBr (△), NaPAA/PAA + NaBr (□), NaPAA/PAA + LiBr (○).

discussing the latter, we shall briefly examine the behavior of PAA in methanol in the presence of Li$^+$ as compared to that of PAA in water with monovalent counterions (e.g., Na$^+$).

It has been shown that for the potentiometric titration of PAA in water, the change of pK with α can be represented by a series expansion up to quadratic or cubic terms in α.[25]

$$pK = pK_0 + \Phi_1\alpha + \Phi_2\alpha^2 + \Phi_3\alpha^3 + \ldots \qquad (6)$$

Here, K_0 represents the (intrinsic) dissociation constant of the acid groups on the macromolecule in the absence of charge effects. The same cubic expansion can also be used for determining K_0 from the titration of PAA in methanol by CH$_3$OLi. The values of pK_0 obtained from the titration of PAA, $M = 5.3 \times 10^5$ g mol^{-1}, in methanol without added salt have been collected in Table I together with the corresponding parameters for the titration of the same sample in water by NaOH. For the former, 13 experimental points in the range $0 \le \alpha \le 0.7$ have been used, and for the latter up to $\alpha = 0.9$. For the titration in methanol in the absence of low molar mass electrolyte, the standard error of estimate S_y of the experimental points with respect to the least-squares cubic polynomial is somewhat larger than the experimental accuracy. As can be seen from this table the low molar mass salt reduces somewhat the value of the parameters both in water and in methanol.

The effect of the solvent on the intrinsic dissociation constant, $\Delta pK_0 \equiv pK_0^* - pK_0$, where the asterisk refers to the value in methanol, is almost equal to that observed for the dissociation constant of acetic acid in the sample couple of solvents, $\Delta pK_d \equiv pK_d^* - pK_d$. At 25 °C the p$K_d$ of this monoacid in methanol has been quoted[26,27] to be $pK_d^* = 9.524$ whereas in water the value $pK_d = 4.756$ is accepted.[28] Therefore $\Delta pK_d = 4.768$ as compared to $\Delta pK_0 = 4.84$ for PAA. Although as pointed out before[25] one should be careful to compare K_0 of a polyacid to K_d of a related monoacid, it is tempting to ascribe ΔpK_0 to a medium effect only. For monoacids, AH, ΔpK_d is defined indeed by[11]

$$\Delta pK_d \equiv pK_d^* - pK_d = \log \frac{\gamma_A{}^t\gamma_H{}^t}{\gamma_{AH}{}^t} \qquad (7)$$

From a theoretical point of view it has been proposed to relate the change of pK with α to the change of the electrostatic surface potential Ψ_s on the polyion[29]

$$pK = pK_0 + 0.434\left|\frac{q\Psi_s}{kT}\right| = pK_0 + 0.434|\phi_s| \qquad (8)$$

where q is the elementary charge and ϕ_s the reduced surface potential. In the case of PAA in water without additional low molar mass electrolyte, the value of $|\phi_s|$ deduced from experimental titration curves with the help of (8) has been compared to theoretical values obtained from the solution of the Poisson–Boltzmann equation for a cell model of a polyion with cylindrical symmetry and uniformly smeared out charge.[30,31] The latter only depends on the value of three parameters, i.e., the concentration of the macromolecule, the radius a of the cylinder representing locally the polyion, and the charge parameter $\lambda \equiv Q/A$, where Q is the Bjerrum length ($Q \equiv q^2/\epsilon kT$) and A is the average contour distance between two successive elementary charges on the real chain. Obviously, A should be proportional to α^{-1}. According to the theory, at constant concentration and a, the value of $|\phi_s|$ should increase monotonously with λ or α. Notwithstanding some reserves that one might have to apply the theoretical model to a polyelectrolyte at very low linear charge density, a reasonable agreement was found for PAA in water between theoretical values of $|\phi_s|$ and values derived from (8), at least if the value $A(\alpha = 1)$ was adjusted to a value somewhat larger than expected from the structure of the macromolecule and if the reasonable value 5.5×10^{-8} cm was assumed for the radius a.[32]

The charge parameter λ^* in methanol with a relative permittivity ϵ_m smaller than the value ϵ_w in water should be larger than the corresponding value of λ in water at the same value of α provided that $A(\alpha = 1)$ is independent of the solvent; i.e., $\lambda^* = (\epsilon_w/\epsilon_m)\lambda$. The solution of the Poisson–Boltzmann equation, if still applicable, would predict that the curve $|\phi_s|$ vs. α in methanol should lie above that in water, the more so if it is assumed that in methanol the value of a may be somewhat larger than in water due to solvation effects. This is not found, however, as can be seen in Figure 15, where $pK^* - pK_0^*$ in methanol and $pK - pK_0$ in water are both presented as a function of α. These curves intersect near $\alpha = 0.3$. This may explain why $\Delta pK_a \equiv pK_a^* - pK_a$, derived from the Henderson–Hasselbalch plots of the titrations of PAA in methanol by CH$_3$OLi and in water by NaOH (see Table I) is somewhat smaller than ΔpK_0 although from the purely electrostatic point of view one would expect a larger value. It follows from (1), (5), and (8) that

$$\Delta pK_a = \Delta pK_0 + 0.434\{|\phi_s^*|_{\alpha=0.5} - |\phi_s|_{\alpha=0.5}\} \qquad (9)$$

(where the reduced potential with and without asterisk refers to the value in methanol and in water, respectively).

As a matter of fact it turns out that it is impossible to fit $pK^* - pK_0^*$ in the range $0 < \alpha < 0.7$ to a theoretical curve according to the solution of the Poisson–Boltzmann equation of the cylindrical cell model in the absence of salt using a constant value for a and $A(\alpha = 1)$. It remains difficult at this stage to explain the much slower increase of $|\phi_s|$ at the higher values of α with respect to the theoretical predictions. Several factors may be responsible for the failure of the simple theory. One possibility is the formation of ion pairs between the carboxylate groups and the Li$^+$ ion resulting in a lowering of the net charge on the

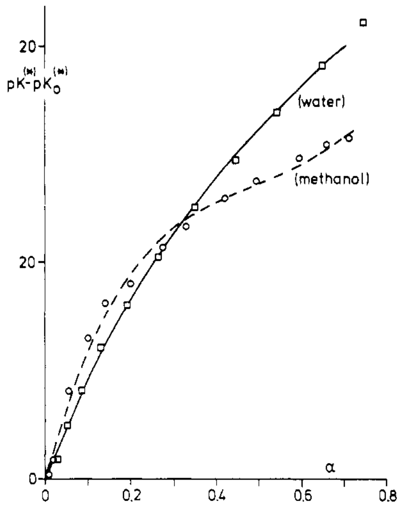

Figure 15. Increase of apparent pK of PAA ($M = 5.3 \times 10^5$ g mol^{-1}) with degree of dissociation α in water ($C_p = 1.50 \times 10^{-2}$ monomol L^{-1}; titrant: NaOH) and in methanol ($C_p = 1.93 \times 10^{-2}$ monomol L^{-1}; titrant: CH_3OLi). The drawn curves represent least-squares fits to eq 6 (see Table I).

macromolecule. The small dimensions of Li^+ and the low value of ϵ_m should favor ion-pair formation in methanol even at average equivalent concentrations that are rather low; the local concentrations of carboxylate groups in the regions occupied by the macromolecular chains will be much higher, and in the absence of additional salt the electrostatic attraction on the Li^+ will be strong. Other factors as well may be of influence, however, as the change with α of the reduced viscosity of PAA in methanol titrated by CH_3OLi cannot be explained by such a reduction of the net charge only.

Whatever the explanation, the change of pK^* (or $|\phi_s|$) with α is monotonous in the presence of Li^+ as the counterion. This is in definite contrast to what is observed when the titration is performed with CH_3ONa. It follows from all three types of representation of the potentiometric titrations that they are consistent with the occurrence of a conformational transition, which shows up as a discontinuity in the region $0.1 \leq \alpha \leq 0.25$. An important observation is the fact that after such a transition is completed ($\alpha > 0.25$) the initial slope of the rise of pK^* with α is larger than before the transition. In the case of PMA in water in the presence of monovalent alkaline counterions, where a conformational transition is also observed,[6] the opposite is true and, together with arguments provided by other experimental techniques, this was interpreted as an indication that the transition occurs between a rather compact average conformation at low degree of dissociation and a more extended one at higher α. In the case of PAA in methanol with Na^+ as counterion, an analogous reasoning would lead to the conclusion that the conformation after the transition is the more compact one.

This last conclusion is supported by viscosity results. The tremendous drop in reduced viscosity within a small α-interval when PAA is titrated in methanol with CH_3ONa is also consistent with a conformational transition from a more or less swollen coil to a more compact structure. It is again contrary to what is observed in the case of aqueous PMA solutions. The near independency of the reduced viscosity on molar mass (especially for higher molar masses) in the case of PAA in methanol for $\alpha > 0.3$ and in the presence of Na^+ is also in agreement with expectations for compact particles. According to the Einstein–Simha equation for solutions of such particles at low concentrations, one has

$$\eta_{sp} = \nu g \qquad (10)$$

where g stands for the volume fraction of the particles and ν is a constant depending on the axial ratio of the spheroidal particle. In the case of a sphere, $\nu = 2.5$. If the particles have constant density d irrespective of their size, the reduced viscosity will be molar mass independent.

$$\eta_{sp}/w = \nu(vN_{Av}/100M) = \nu(|d^{-1}|/100) \qquad (11)$$

Here, v is the volume of a single particle and N_{Av} represents Avogadro's constant. Equation 11 has been applied to globular proteins[19] to estimate their average dimensions in solution. For PAA in methanol at $\alpha = 0.3$ and with Na^+ as counterion the same is, in principle, also possible. If, for example, for the sample $M = 5.5 \times 10^5$ g mol^{-1} we neglect in a first approximation the observed small concentration effects (probably due to dissociation effects) and use an average value $\eta_{sp}/w \simeq 0.14$ dL g^{-1}, the hydrodynamic radius R_H is found to be of the order of 10^{-6} cm assuming a spherical shape ($v = 4\pi R_H^3/3$). This is nearly the same value as the root-mean-square radius of gyration of a random flight chain with $N = 7.6 \times 10^3$ elements of length $l = 2.5 \times 10^{-8}$ cm, which would be the absolute lower limit of the root-mean-square radius of gyration of PAA under unperturbed conditions (Θ-conditions). Under those conditions the root-mean-square radius of gyration should increase however with $M^{1/2}$ as found for unneutralized PAA in aqueous 0.01 M HCl indeed. As this is not the case here it may be tentatively concluded that PAA after the conformational transition, occurring at room temperature in methanol in the presence of Na^+, is in a collapsed conformation as predicted below the Θ-temperature. Note that at present we do not know whether or not this collapsed conformation is spherical.

Such a collapse does not seem to occur in the presence of Li^+ as counterions. Although as pointed out above the reduced viscosity also strongly decreases after a maximum situated around $\alpha = 0.25$, this decrease occurs over a broad α-interval and the reduced viscosity never reaches the extreme small values observed with Na^+ after the conformational transition.

Qualitatively, the behavior of PAA in methanol for $\alpha < 0.1$ does not differ whether it is titrated by CH_3OLi or by CH_3ONa. This can be seen from the viscosity measurements on PAA solutions (Figures 9 and 12) without salt or by the influence of salt on the viscosity (Figure 14). It is also revealed by the potentiometric titrations, e.g., in the parameters of the Henderson–Hasselbalch representation. For $\alpha < 0.1$ the values of $(pK_a^*)_1$ and n_1^* in the presence of Na^+ are in good agreement with pK_a^* and n^* in the presence of Li^+ (see Table I). After the transition in the presence of Na^+ the values of both pK_a^* and n^* increase in the absence or in the presence of salt. Even more surprising is the much higher value of n_2^* after salt has been added. Such an increase is quite abnormal and is specific for Na^+. Note that in the case of PMA in water the lower values of n and pK_a are found in the neutralization region after the transition and that there the effect of added salt is to lower the value of n.

It may be concluded from the potentiometric and viscosimetric titration of poly(acrylic acid) in methanol at room temperature that it behaves differently above $\alpha > 0.1$ in the presence of Na^+ as counterion as compared to Li^+. Such a difference in qualitative nature has not been observed for comparable titrations in water in the presence of different alkaline counterions where only small quantitative deviations have been found. The results obtained here suggest that PAA in the presence of Na^+ undergoes a conformational transition in a small interval of degree

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of dissociation, $0.1 \le \alpha \le 0.25$, 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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