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Solvent Effects in Polyelectrolyte Solutions. 3. Spectrophotometric Results with (Partially) Neutralized Poly(acrylic acid) in Methanol and General Conclusions regarding These Systems

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ABSTRACT: Absorption measurements in the near-UV of partially neutralized poly(acrylic acid) (PAA) in methanol at room temperature again confirm that these solutions behave qualitatively differently if Na^+ is the counterion than if Li^+ is the counterion, at least for degrees of dissociations $\alpha > 0.10$. Although in both cases some of the effects observed may be attributed to ion pairing, no inconsistency with the occurrence of a conformational transition for NaPAA/PAA around $\alpha = 0.15$ is found. In the general discussion the importance of the solvent quality for understanding these properties is stressed, which is determined not only by the macromolecular chain and its functional groups but in polyelectrolyte solutions also by the nature of the counterion. It is postulated that in methanol at room temperature slightly neutralized PAA is already near Θ-conditions. Increasing the degree of neutralization probably increases the Θ-temperature of the systems depending on the nature of the counterions, the increase being faster when Na^+ is the counterion than when Li^+ is the counterion. In the presence of Na^+ a collapse of the chain into a compact particle with low net charge occurs, which qualitatively may be understood by the condensation avalanche effect proposed by Khokhlov. The better solvation of Li^+ in methanol seems to prevent the same effect if PAA is neutralized by CH_3OLi at room temperature.

I. Introduction

It has been shown in the previous papers (parts 1 and 2) that the physicochemical behavior of partially neutralized poly(acrylic acid) (PAA) in methanol at room temperature is determined to a great extent by the nature of the alkali metal counterion present in the solution. When titrated with CH_3ONa, PAA seems to undergo a conformational transition in the range of degree of dissociation $0.10 < \alpha < 0.25$. No such conformational transition was observed over the course of the titration with CH_3OLi. But in the latter the change of several experimental quantities with respect to those in the titration of PAA in water suggests that other than purely electrostatic effects in terms of the classic polyelectrolyte theory may (partially) be responsible for these changes. It may therefore be interesting to investigate whether in both cases specific interactions between ionized groups on the polyion and the counterions may be in part responsible for the observed behavior. In general, spectroscopic methods can be used to study such interactions, in particular if they involve binding or change in solvation of the absorbing group(s). A quantitative analysis is possible only whenever the extinction coefficients of all species involved can be determined independently of each other.

The near-UV absorption of carboxyl and carboxylate groups of PAA in methanol and its dependence on the degree of dissociation, counterion, molar mass, and concentration have therefore been studied. In the case of a simple acid–base equilibrium when only two absorbing species, represented by AH and A^-, are present, the absorbance at a given wavenumber σ, $A(\sigma)$, will depend linearly on the degree of dissociation according to the equation

$$A(\sigma) = bC\{\epsilon_{AH}(\sigma) + \alpha[\epsilon_{A^-}(\sigma) - \epsilon_{AH}(\sigma)]\} \qquad (1)$$

Here, $\epsilon_i(\sigma)$ represents the molar extinction coefficient of species i at wavenumber σ, C the total concentration of the acid, and b the path length. In the case of a polyacid with monomolar concentration C_p in which each monomeric unit carries an acid group, this leads to the following expression for the reduced absorbance $\bar{A}$.

$$\bar{A}(\sigma) \equiv \frac{A(\sigma)}{bC_p} = \epsilon_{AH}(\sigma) + \alpha[\epsilon_{A^-}(\sigma) - \epsilon_{AH}(\sigma)] \qquad (2)$$

Equations 1 and 2 imply the existence of an isosbestic point at a wavenumber where $\epsilon_{AH} = \epsilon_{A^-}$. Such an isosbestic point has indeed been found over the complete range of titration for PAA in water, and eq 2 was confirmed.[3–7] For the titration of PMA in water, the linear relation (2) was not obeyed but the reduced absorbance could be interpreted in terms of the conformational transition that poly(methacrylic acid) undergoes over the course of its titration.[4] The same approach will be followed in the discussion of the spectrophotometric titration of PAA in methanol at room temperature. At the end of that discussion we shall present a survey of all the experimental evidence obtained so far and a tentative interpretation for the behavior of PAA in methanol.

II. Experimental Section

Poly(acrylic acid), methanol, and the methoxides were as described in part 1.

Spectra were recorded with a double-beam DMR 21 spectrophotometer (Carl Zeiss, Oberkochen), and absorbances at fixed wavenumbers were measured with a single-beam PMQ II spectrophotometer (Carl Zeiss, Oberkochen). UV precision cells with Teflon stoppers were used; path lengths were 0.1, 0.2, 0.5, and 1.0 cm, depending on the polymer concentration. The temperature was kept constant at 20 °C.

Samples were obtained either by preparing a range of solutions of fixed C_p at different α before the measurements or by weighing a poly(acrylic acid) and a polyacrylate stock solution in different proportions in a cuvette. The absorbance appeared to be independent of the preparation procedure used.

Careful correction for the absorbance of the solvent was necessary at the wavenumbers investigated as methanol absorbs already considerably above 45 000 cm^{-1}. In addition, the absorbance of O_2 present in the solution interferes with the spectrum of methanol.[8,9] However, it was not easy to perform measurements under a nitrogen atmosphere with the experimental setup used. For these reasons quantitative measurements have been carried out from 44 000 to 48 000 cm^{-1} on rather concentrated solutions. Reproducibility under these conditions was found to be within 4%. For such concentrations methanolysis could also be neglected.

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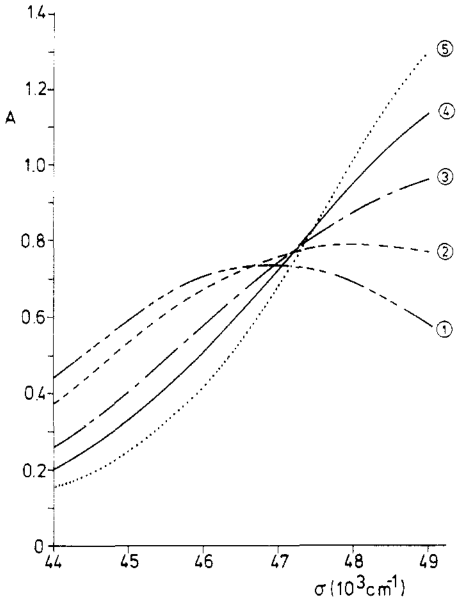

Figure 1. Absorbance vs. wavenumber σ for PAA ($M = 5.7 \times 10^4$ g mol^{-1}) in methanol ($C_p = 3.81 \times 10^{-2}$ monomol L^{-1}) partially neutralized by CH_3ONa: (1) $\alpha = 0.00$; (2) 0.15; (3) 0.45; (4) 0.70; (5) 0.90. Path length 0.2 cm.

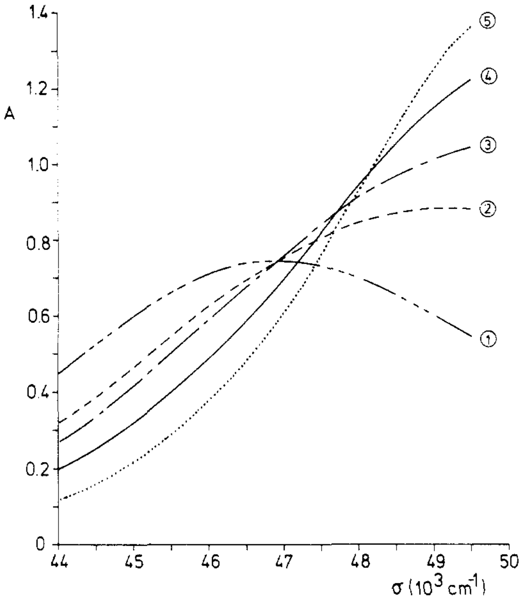

Figure 2. Absorbance vs. wavenumber for PAA ($M = 5.7 \times 10^4$ g mol^{-1}) in methanol ($C_p = 3.81 \times 10^{-2}$ monomol L^{-1}) partially neutralized by CH_3OLi: (1) $\alpha = 0.00$; (2) 0.32; (3) 0.46; (4) 0.66; (5) 0.85.

III. Results

In Figures 1 and 2, spectra of PAA ($M = 5.7 \times 10^4$ g mol^{-1}) in methanol partially neutralized with CH_3ONa or CH_3OLi to different degrees of dissociation are presented. For comparison analogous spectra for acetic acid in methanol are given in Figure 3. For the acetic acid/acetate mixtures the spectra exhibit an isosbestic point over the complete range of degree of dissociation. For the case of poly(acrylic acid)/polyacrylate the isosbestic point is only present for a limited range of α-values, which is broader if Li^+ is the counterion than if Na^+ is the counterion.

The presence of more than two absorbing species at higher α for PAA in methanol is clearly demonstrated by the plots of $\bar{A}$ vs. α in Figures 4 and 5. Results at four different wavenumbers are presented for PAA of two molar masses and of different concentrations. No straight lines are obtained, at least at two wavenumbers for the systems considered. Special concentration effects cannot be observed however. In that connection it should be mentioned that concentration-dependent interactions do not seem to influence the absorbance, as the Lambert–Beer law has been found to hold over the concentration range 5×10^{-3} to 10^{-1} monomol L^{-1}. It should also be noticed that the deviations from the linearity in the plots $\bar{A}$ vs. α always correspond to a reduction in the absorbance and therefore cannot be attributed to impurities.

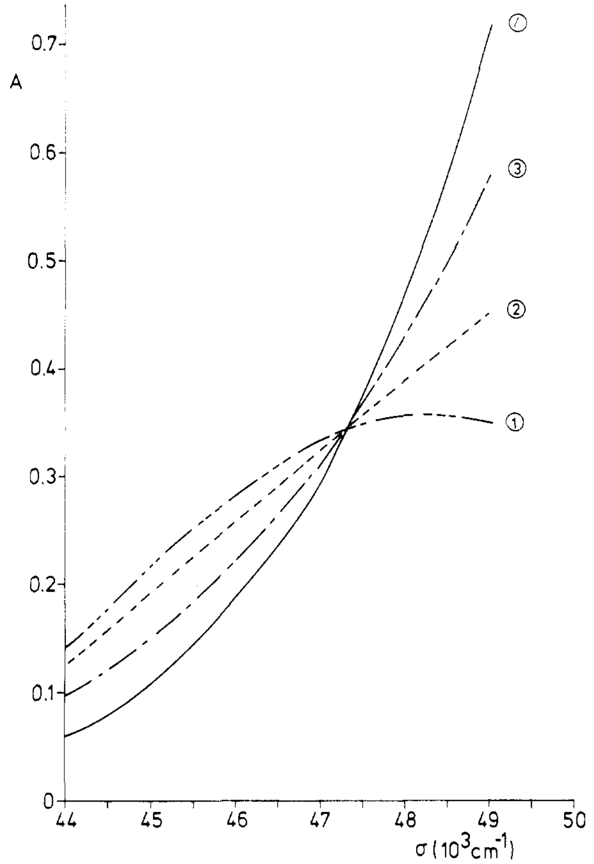

Figure 3. Absorbance vs. wavenumber for acetate/acetic acid mixtures in methanol ($c = 4.90 \times 10^{-2}$ M) at different ratios r: (1) $r = 0.00$; (2) $r = 0.20$; (3) $r = 0.50$; (4) $r = 0.80$. Path length 0.2 cm.

It is interesting that the absorbance of PAA of very low molar mass ($P = 75$) titrated by CH_3ONa does *not* exhibit such deviations at the four wavenumbers considered, as shown in Figure 6. For the two other, higher, molar masses the deviations from linearity start at different values of α for Na^+ and Li^+ as counterions, in agreement with the observation concerning the isosbestic point. For Na^+ a significant change in the slope of $\bar{A}$ vs. α can be detected at 47 000 and 48 000 cm^{-1} around $\alpha = 0.3$. For higher values of the degree of dissociation, again a straight line is found. For Li^+ an analogous change is observed around $\alpha = 0.5$ but here the deviations are no longer confined to the largest wavenumbers considered and also $\bar{A}$ does not seem to depend linearly on α for $\alpha > 0.5$.

If we compare the slopes that can be calculated from a least-squares fit to a straight line for $\alpha < 0.3$ with both kinds of counterions, we find a fairly good agreement as shown in Table I. We can also determine the molar extinction coefficients for the carboxyl and the carboxylate groups for PAA in methanol in the range of α values starting from $\alpha = 0$ where no deviations from linearity can be detected with (2) (see Table I). It can be seen that the values for ϵ_{COOH} for solutions containing Na^+ are in good agreement with those of solutions containing Li^+. The

Table I
Slopes of the Lines $\bar{A}$ vs. α and Values of the Molar Extinction Coefficients (L monomol^{-1} cm^{-1}) of Carboxyl Acid Groups -COOH and Carboxylate Groups -COO$^-$ of PAA ($M > 57 \times 10^3$ g mol^{-1}) in Methanol at 20 °C^a

	Na$^+$			Li$^+$		
wavenumber, cm^{-1}	slope^b	ϵ_{COOH}^{c}	ϵ_{COO^-}^{c}	slope^b	ϵ_{COOH}^{d}	ϵ_{COO^-}^{d}
45000	-60 ± 3	78.1 ± 0.4	28 ± 1	-57 ± 3	80.6 ± 0.4	23 ± 2
46000	-36 ± 2	94.9 ± 0.4	53 ± 1	-38 ± 3	94.6 ± 0.4	55 ± 2
47000	9 ± 2	97.9 ± 0.4	106 ± 3	4 ± 2	98.7 ± 0.3	99 ± 1
48000	70 ± 3	91.4 ± 0.5	161 ± 4	59 ± 3	92.3 ± 0.4	148 ± 2

[a] All errors indicated are standard deviations as computed from least-squares fittings. [b] Slope calculated for $\alpha < 0.3$. [c] From values in the region $0 < \alpha < 0.9$ for the two lower wavenumbers and in the region $0 < \alpha < 0.3$ for the two higher wavenumbers. [d] From the values in the region $0 < \alpha < 0.5$.

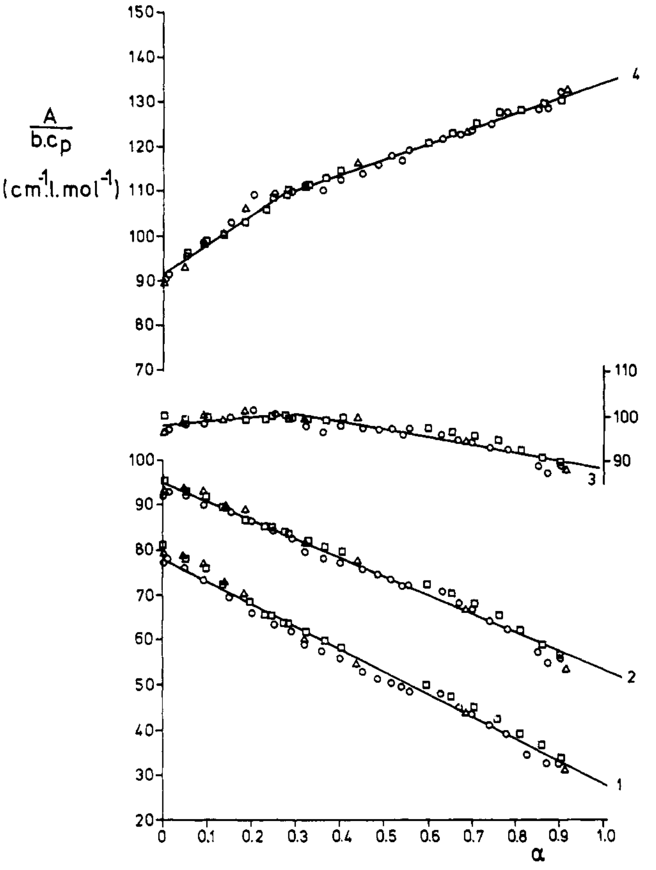

Figure 4. Reduced absorbance vs. degree of dissociation α for PAA in methanol partially neutralized by CH_3ONa at 45000 (1), 46000 (2), 47000 (3) (ordinate at the right), and 48000 (4) cm^{-1}. Various systems investigated: (△) $M = 5.3 \times 10^5$ g mol^{-1}, $C_p = 8.70 \times 10^{-2}$ monomol L^{-1}; (○) $M = 5.7 \times 10^4$ g mol^{-1}, $C_p = 3.80 \times 10^{-2}$ monomol L^{-1}; (□) $M = 5.7 \times 10^4$ g mol^{-1}; $C_p = 4.6 \times 10^{-3}$ monomol L^{-1}.

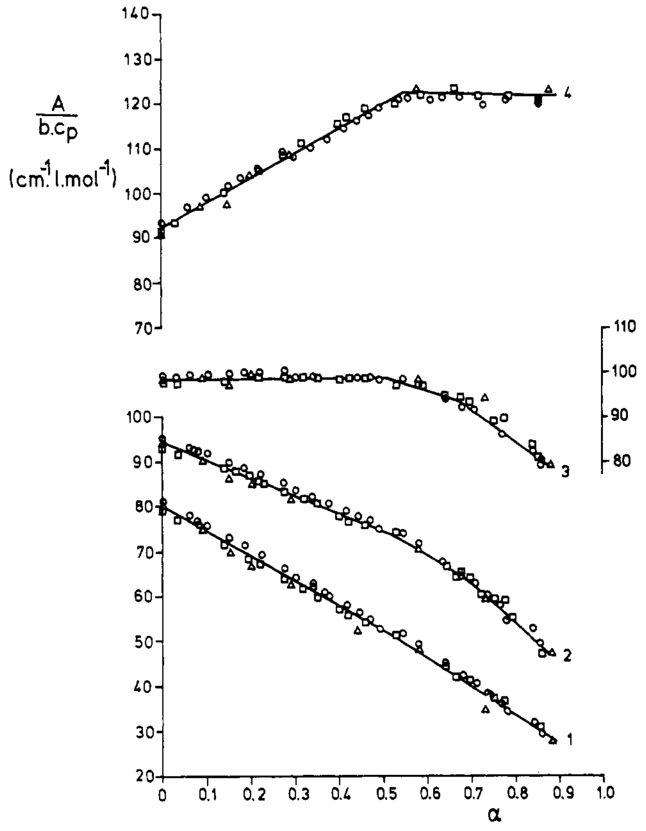

Figure 5. Reduced absorbance vs. degree of dissociation for PAA in methanol partially neutralized by CH_3OLi at 45000 (1), 46000 (2), 47000 (3) (ordinate at the right), and 48000 (4) cm^{-1}. Various systems investigated: (△) $M = 5.3 \times 10^5$ g mol^{-1}, $C_p = 8.70 \times 10^{-2}$ monomol L^{-1}; (○) $M = 5.7 \times 10^4$ g mol^{-1}, $C_p = 2.29 \times 10^{-2}$ monomol L^{-1}; (□) $M = 5.7 \times 10^4$ g mol^{-1}, $C_p = 3.81 \times 10^{-2}$ monomol L^{-1}.

agreement for ϵ_{COO^-} is less good but still fair enough to conclude that for $\alpha < 0.3$ no significant specific effects due to the difference in counterions can be detected spectrophotometrically. These specific effects only appear at higher values of the degree of dissociation, in agreement with the results with other physicochemical techniques.

For $\alpha > 0.3$ the following differences between the curves $\bar{A}$ vs. α for PAA in methanol in the presence of Na$^+$ or Li$^+$ can be observed. For the former no deviations from linearity can be detected at 45000 and 46000 cm^{-1}, and the intercepts with the y axis of the two linear portions at 47000 and 48000 cm^{-1} do not differ by more than 10%, indicating that the changes in slopes are rather small. In the case of Li$^+$ the changes are much more important at the wavenumbers 46000, 47000, and 48000 cm^{-1}. It is therefore unlikely that in both kinds of systems the deviations from linearity, although all negative, can be ascribed to exactly the same causes.

IV. Discussion

As discussed in parts 1 and 2, the change of many physicochemical properties of PAA in methanol neutralized by CH_3ONa at room temperature points to the possibility that PAA undergoes a conformational transition from a more or less expanded coil to a compact particle in the range $0.1 < \alpha < 0.25$. The changes in the slope in the straight lines $\bar{A}$ vs. α at 47000 and 48000 cm^{-1} occur around $\alpha = 0.3$, i.e., around the degree of dissociation at which this transition should be completed. It may therefore be related to the changes in the direct environment of the absorbing groups, i.e., changes in solvation and eventually formation of some kind of ion pairs inside the compact particle with respect to the macromolecule in its more coil-like conformation. The fact that the low molar mass PAA does not exhibit any spectrophotometrically observable changes is probably due to the impossibility of forming a compact particle at low degree of polymerization (see also the results of the conductometric titrations).

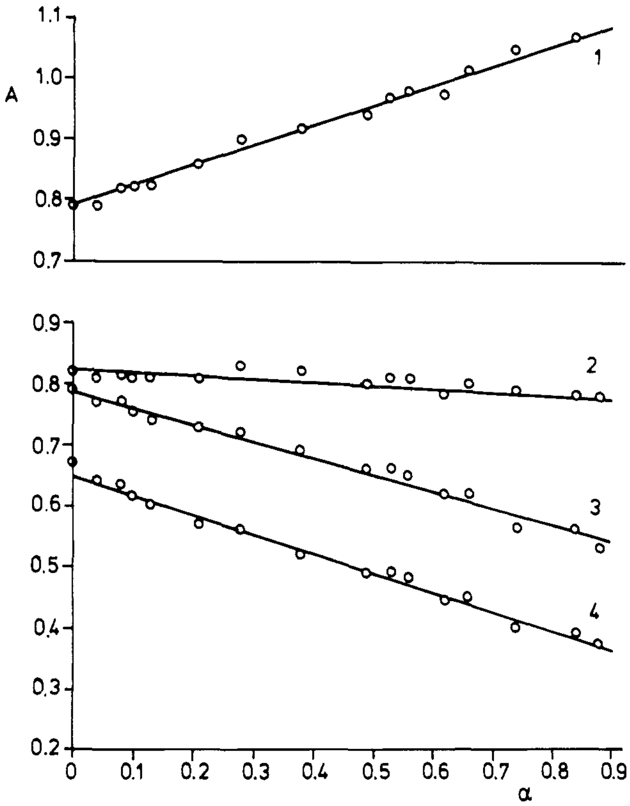

Figure 6. Absorbance vs. degree of dissociation of PAA (M = 5.3 × 10^3 g mol^{-1}) in methanol (C_p = 3.82 × 10^{-2} monomol L^{-1}) at 48 000 (1), 47 000 (2), 46 000 (3), and 45 000 (4) cm^{-1}.

Experiments with other techniques lead to the conclusion that at room temperature the conformational transition does not seem to occur during the titration of PAA in methanol by CH_3OLi. The deviations from linearity of the curves $\bar{A}$ vs. α appear in the range of α values where also considerable reduction in the values of other physicochemical quantities have been observed with respect to the values in water which could not be understood on the bases of classical polyelectrolyte theory considering the increase of the charge parameter λ only. (See, e.g., the potentiometric, viscosimetric, and osmometric titrations in the presence of Li^+.) It may be conjectured that these deviations may be related to the formation of ion pairs of Li^+ with the carboxylate groups, which should reduce the net charge on the macromolecule and affect the absorption in the near-UV of the carboxylate group. It has been suggested from the comparison of the values of activity coefficients of alkali metal acetates in aqueous solutions that Li^+ has a larger tendency for ion pairing than other alkali metal ions.[10,11] The effects are observed only in rather concentrated solutions. For polyelectrolytes, however, due to the high "local" concentration of functional groups, ion pairing might be expected to occur at low average concentrations, particularly in a solvent with smaller relative permittivity than water.[1] This ion pairing will be more pronounced the higher the concentration of lithium carboxylate and the higher the value of α. Unfortunately, a more quantitative analysis of the curve $\bar{A}$ vs. α at $\alpha >$ 0.5 remains difficult, as the extinction coefficient of the ion pair cannot be determined independently.

If the explanation just proposed is correct, it would follow that the specific differences between the behavior of PAA in methanol at room temperature in the presence of Li^+ and of Na^+ cannot be attributed to the formation of ion pairs only (the deviations from linearity in the presence of Na^+ being also qualitatively different from those observed in the presence of Li^+), but this does not exclude the possibility that the postulated transition to compact particles for $\alpha > 0.1$ in the presence of Na^+ (and not in the presence of Li^+) is accompanied to some extent by ion pairing.

Turning to a more general discussion, we point out an interesting analogy between the solution behavior of methanolic PAA in the postulated compact state in the presence of Na^+ and that of lyophobic colloids (e.g., suspension of latex particles). These colloids remain in suspension, i.e., do not flocculate because of their surface charge.[12] Flocculation can however occur by addition of small amounts of salt. Because the colloids can never be prepared directly by dissolving the dry material in the solvent, sometimes the name "irreversible colloids" is used. The viscosity of these systems does not differ much from that of the solvent (Einstein's formula can be applied) and visible light is strongly scattered, leading sometimes to opalescence of the suspensions. These phenomena have also been observed for methanolic PAA at room temperature in the presence of Na^+ for $\alpha > 0.3$. To confirm the irreversible behavior, enough NaBr was added to such a solution for phase separation to occur. It was then exhaustively dialyzed against pure methanol but when all the salt had been extracted, the phase separation did not disappear. This additionally supports the hypothesis that after the conformational transition observed in the presence of Na^+, poly(acrylic acid) becomes a compact particle with a small surface charge, in agreement with other experimental findings.

All the results of the present investigation are consistent with the assumption that PAA in methanol at room temperature and without added salt exhibits a conformational transition in the range $0.10 < \alpha < 0.25$ in the presence of Na^+ as counterion. This transition leads to compact particles with only a small surface charge and most carboxylate groups and counterions contained within the particle and to a solution that is probably under metastable conditions. In the presence of Li^+ this conformational transition is not observed but some solvent specific effects also do occur, particularly for $\alpha > 0.5$, which may be partially connected to ion pair formation. The experimental evidence available does not as yet permit any conclusion about the effect of the small amount of water present in the solutions investigated.

Polyacrylate systems under different experimental conditions have already been found to exhibit a behavior that can be interpreted by assuming a collapse of the charged macromolecular chain into a compact particle upon titration. PAA solutions in ethanol–water mixtures at room temperature and without added salt have been investigated as a function of the composition in the presence of K^+ as the counterion by Muresan and Zador.[13-17] Plots of the specific conductance,[16] specific viscosity,[14] and pH[13,15] vs. α' in mixtures with low ethanol content resemble those observed here for PAA with Li^+ in methanol. When the ethanol content is increased, the plots show more and more resemblance to those found in methanol but with Na^+ as counterion. The authors conclude that with increasing α' a conformational transition occurs when the ethanol content is high because "unfavorable enthalpic interactions are responsible for the insolubility of K(PAA) in absolute ethanol" and "the globule form assures a lower interaction energy between –COOK groups and solvent molecules by hiding a larger fraction of –COOK in the interior of the globule away from the solvent molecules".

Investigations by Wojtczak[19-22] on aqueous solutions of PAA without added salt in the presence of either Ca^{2+} or

Table II
Thermodynamic Data of Alkali Metal Chlorides in Methanol at 25 °C[a]

salt	$\Delta H^\circ_{\text{lat}}$[b]	$\Delta H^\circ_{\text{s}}$	$\Delta H^\circ_{\text{solv}}$[c]	solubility[e]
LiCl	−846.3	−48.1[b]	−894.4	9.7
NaCl	−777.8	−8.8[b]	−786.6	0.24
KCl	−706.7	+3.3[d]	−703.4	0.07

[a] Enthalpies in kJ mol^{-1}; solubilities in mol L^{-1}. [b] Data computed from NBS values.[22] [c] Data computed according to (3). [d] Data taken from ref 23. [e] Data taken from ref 24.

Ba^{2+} as counterion show for these solutions a behavior analogous to that observed here. E.g., the reduced viscosity η_{sp}/w of PAA in the presence of Ba^{2+} in water changes with increasing α in the same way as η_{sp}/w in methanol in the presence of Na^+. Conversely, in the presence of Ca^{2+} the change of the reduced viscosity in water is comparable to that of PAA in methanol when Li^+ is the counterion. According to Wojtczak, PAA exhibits a conformational transition from a coil to a hypercoil with increasing α in the presence of Ba^{2+}. This transition sets in at a lower value of α' at a lower temperature as concluded from potentiometric titrations performed at several temperatures between 5 and 50 °C.[22] Wojtczak assumes strong hydrogen bonds between the carboxylic and the carboxylate groups to stabilize the hypercoil but this explanation leaves many of the observed effects unexplained.

Both series of investigations together with our results in methanol however show that at a given temperature the physicochemical behavior of polyacrylates as a function of the degree of ionization is determined both by the solution properties of the macromolecular chain and its functional groups and by its counterions. Conversely, the conformational transition as observed in all these systems strongly depends on the nature of the solvent, the degree of dissociation (or charge of the macromolecular chain), the nature of the counterion and the temperature. It must occur under experimental conditions where intramolecular attractions become dominant in spite of the strong charge repulsions along the polymer chain and therefore must be related to solvent quality effects. It is highly probable that this transition takes place below Θ-conditions, which are probably reached in methanol at room temperature when in the presence of Na^+ poly(acrylic acid) is progressively charged because the quality of methanol as a solvent decreases with respect to that for neutral PAA. It is easy to understand that besides the interaction of the macromolecular chain and methanol also the interactions between the counterion and the solvent play an important part in determining the thermodynamic conditions for the Θ-temperature. In this respect it is interesting to compare solvation data for Li^+ and Na^+ in the presence of the same anion in methanol at room temperature. Unfortunately, free energy of solvation values cannot be estimated from the information available but the standard enthalpy $\Delta H^\circ_{\text{solv}}$ for bringing a cation and anion from vacuum into the solvent can be calculated from data in the literature.

$$\Delta H^\circ_{\text{solv}} = \Delta H^\circ_{\text{s}} + \Delta H^\circ_{\text{lat}} \tag{3}$$

Here, $\Delta H^\circ_{\text{s}}$ stands for the standard enthalpy of solution (crystal → solution) and $\Delta H^\circ_{\text{lat}}$ the standard lattice enthalpy (ions in vacuum → crystal). In Table II values of these quantities have been collected for alkali metal chlorides in methanol at 25 °C. When comparing these data one can see that the enthalpy of solvation is more favorable in the case of Li^+ than in the case of Na^+ or K^+. From the same table it also appears that $\Delta H^\circ_{\text{s}}$ values increase when going from LiCl to KCl in a parallel way to the decrease of the solubility of these salts. The same order of solubility with increasing alkali metal cation radius has been found for alkali metal carboxylates in methanol.[25,26]

Although we have no information about possible entropic effects, it is tempting to conclude from the less negative solvation enthalpy for Na^+ as compared to that for Li^+, from the lower solubility of carboxylates in alcohols compared to water,[27] and from the decreasing solubility of carboxylates with increasing alkali cation radius, that methanol will be a poor solvent for (partially) neutralized poly(acrylic acid) (see also ref 18 and 27) and that the solvent quality will decrease under comparable conditions when Li^+ is replaced by Na^+.

Recently, a theory on the conformational transition from coils to globules for weakly charged polyelectrolytes in salt-free solutions near Θ-conditions has been proposed by Khokholov.[28] We shall briefly summarize this theory, which can explain qualitatively the effects observed for PAA in methanol when neutralized by CH_3ONa, although we do not have enough evidence to prove that the conditions under which Khokhlov's theory is valid are really met in our experiments.

Consider an uncharged wormlike chain with contour length l and persistence length L near the Θ-temperature in the dilute regime where the macromolecule behaves as an ideal Gaussian coil. Lowering the temperature below Θ will result in the collapse of the chain at a temperature T_1, which is sufficiently close to Θ so that the reduced temperature τ, defined by

$$\tau = (\Theta - T)/\Theta \tag{4}$$

corresponding to T_1, i.e., τ_1, satisfies the condition $0 < \tau_1 \ll 1$. If the polymer is now slightly charged under Θ-conditions for the neutral polymer in such a way that the charges are distributed uniformly along the chain but the resulting electrostatic interactions can be viewed as a small perturbation only (weak-coupling limit), the polyelectrolyte can be represented by a "blob" model (for the concept of blobs see, e.g., ref 29). In the dilute regime, which must satisfy the condition $n_{\text{p}} \ll PR_q{}^3$, where n_{p} represents the average concentration in monomeric units per unit volume and R the average extension of the polyelectrolyte with degree of polymerization P, the screening of the macromolecular charges by the counterions is very ineffective. Inside the blobs the electrostatic perturbation is too weak to affect the average conformation of the chain, which retains its Gaussian character. Between the blobs, which carry each $g \gg 1$ elementary charges q, sufficient repulsion occurs to make the blobs pile up into an extended conformation. Therefore for $T_1{}^\circ < T < \Theta^\circ$ (where the superscript refers to characteristic temperatures of the *neutral* polymer) the average dimensions of the blobs have to satisfy the two conditions

$$D_{\text{c}} \simeq g^2 Q \simeq (L^\circ ga/\alpha)^{1/2} \tag{5}$$

where Q stands for the Bjerrum length, $Q \equiv q^2/4\pi\epsilon\epsilon_0 kT$, a for the length of a monomeric unit, L° for the persistence length of the neutral macromolecule (which is assumed to remain unaffected by the weak charge interactions). Note that g/α represents the number of monomers inside a blob. Under the same conditions the average extension of the polyelectrolyte is given by

$$R_{\text{c}} \simeq (P\alpha/g)D_{\text{c}} \tag{6}$$

In (5) and (6) the symbol $\simeq$ means equal to within a factor of order unity and it has been assumed that each monomeric unit bears an elementary charge if the polyelectrolyte is fully charged.

If the temperature is lowered to $T_1{}^\circ$, the chain portions inside the blobs will collapse but the piling of the blobs will persist. This will result in a reduction of the average blob dimensions from D_c to D_g and of the average extension of the macromolecule from R_c to R_g.

$$D_g \simeq (a/L^\circ)^{1/2} D_c \qquad \tau \ge \tau_1^\circ \tag{7}$$

$$R_g \simeq (a/L^\circ) R_c(\tau_1^\circ/\tau) \qquad \tau \ge \tau_1^\circ \tag{8}$$

The collapse inside the blob thus reduces the asymmetry R/D of the rodlike conformation by a factor $(a/L^\circ)^{1/2} \cdot (\tau_1^\circ/\tau)$ depending on temperature.

The dilute regime to which these expressions should be applicable is in practice unattainable[30-32] and most experiments on polyelectrolytes without added salt are performed in the semidilute regime, where according to Khokhlov the average monomer concentration in solution will still be smaller than the average monomer concentration inside a single blob. In this regime some overlap between chains and screening by counterions become effective and each polyelectrolyte chain may be viewed as a chain with an effective degree of dissociation $\alpha_{\text{eff}} = \alpha f \le \alpha$. The linear charge density σ of the polyion still assumed to be a rodlike pile of blobs, will depend on the way the screening affects the average extension $R(f)$.

$$\sigma(f) = \alpha f P/R(f) \tag{9}$$

In order to estimate the influence of the screening, Khokhlov resorts to Oosawa's theory based on a two-phase model,[33] which for low values of the volume fraction ϕ (with $\phi \ll 1$ in the semidilute regime) yields the following expression for f.

$$\ln [(1-f)/f] \simeq [1 - Q\sigma(f)] \ln \phi \qquad \phi \ll 1 \tag{10}$$

For $0 < \tau < \tau_1^\circ$, using the expression for R_c derived in the case of the dilute regime (6) but with α replaced by αf, it can be shown that $Q\sigma(f) \ll 1$ and consequently $f \simeq 1$; i.e., the average dimensions in the semidilute regime will be comparable to those of the dilute regime under these conditions with R_c a slowly increasing function of α. Lowering of the temperature below T_1° leads again to a collapse inside the blobs but this causes f to decrease from unity. For $\tau \ge \tau_1^\circ$ the linear charge density increases with decreasing temperature according to $\sigma(f) \sim \tau f^{-1/3}$. This follows from (6) and (8), assuming again that the equations established for the dilute regime may be used with α replaced by αf. By a further slight decrease of the temperature a stage is reached where for $T_2 < T_1^\circ$ the condition $Q\sigma(f) = 1$ is satisfied. No physically acceptable solution for (10) then exists and an unstable situation sets in. In this situation any very small increase of the linear charge density as a result of a very small decrease of f as required by (10) leads to a further lowering of f and thus a subsequent increase of $\sigma(f)$. According to Khokhlov this can be viewed as a *condensation avalanche effect*: at $\tau \ge \tau_2$ condensation of counterions reducing the effective charge on the polyion causes a reduction of the average extension overcompensating the latter and therefore further condensation of counterions. This avalanche only stops when the average extension of the polyelectrolyte chain has reached a sufficiently small value as to meet the conditions for the dilute regime where further condensation or screening no longer occurs. Finally, a compact, globule-like particle results with a very low effective charge. This residual charge prevents phase separation in spite of the strong attractions between macromolecular segments inside the globule, just as is the case with lyophobic colloids.

We believe that the collapse accompanied by an avalanche type of condensation in the semidilute regime of weakly charged polyelectrolytes as described by Khokhlov could possibly explain the conformational transition observed with PAA in methanol at room temperature around $\alpha = 0.15$ when the polyacid is neutralized by CH_3ONa. Though lowering of the temperature would be the usual method to reach Θ-conditions and to increase τ, the same effects could be obtained upon charging the polymer chain and increasing the number of counterions in solution at constant temperature, provided this strongly affects the quality of the solvent. At present, not enough experimental evidence is available to verify whether or not the conditions for Khokhlov's theory to apply are met and to test in a more quantitative way the predictions of the theory. It should be observed that this theory itself presents some flaws, the use of Oosawa's theory based on the two-phase assumption being not a minor one.

We conjecture that upon neutralizing PAA in methanol, which at room temperature is already not a good solvent for the uncharged polyacid, two effects have to be taken into account. On the one hand, carboxylic acid groups dissociate and electrostatic interactions increase just as is the case in aqueous solutions. On the other hand, the potential of mean force between segments on the chain changes also insofar as the contribution of not purely electrostatic interactions is concerned (a contribution that cannot be neglected here but is negligible in a good solvent) with a subsequent increase in the Θ°-temperature, i.e., the Θ temperature as determined by the macromolecule and the counterions if their electric charge would be removed. In the case of PAA neutralized by CH_3ONa, but not with CH_3OLi, this Θ°-temperature rises around $\alpha = 0.15$ above the temperature at which the experiments are being performed, leading to a collapse analogous to that described by Khokhlov. According to his theory,[28] a minor decrease of T below Θ° is sufficient for effectuating the collapse with the avalanche-type condensation. Therefore in our case a small difference in the thermodynamic properties should already explain the difference in solution behavior of PAA neutralized by CH_3ONa and by CH_3OLi. Note that Khokhlov's theory is only applicable if the contour length satisfies certain conditions that will not be met for polyelectrolytes of low molar masses. This is consistent with the observation that the conformational transition of PAA in methanol could not be observed upon neutralization with CH_3ONa for $P \le 800$ (see also part 2).

Finally, it is quite possible that the results of K(PAA) in ethanol–water mixtures as well as those of PAA in aqueous solutions in the presence of Ba^{2+} and Ca^{2+} could also be understood analogously in terms of Khokhlov's theory. The observation that in the latter the transition observed in the presence of Ba^{2+} starts at lower values of α when the temperature is lowered is consistent with this point of view. It remains however that further systematic investigations in all systems considered are necessary before a more definite conclusion can be reached.

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Registry No. PAA, 9003-01-4; LiCl, 7447-41-8; NaCl, 7647-14-5; KCl, 7447-40-7; PAA·Na, 9003-04-7; PAA·Li, 25656-42-2.

References and Notes

(1) Davies, C. W. "Ion Association"; Butterworths: London, 1962.
(2) Jaffé, H. H.; Orchin, M. "Theory and Application of Ultraviolet Spectroscopy"; Wiley: New York, 1962.
(3) McDiarmid, R.; Doty, P. *J. Phys. Chem.* **1966**, *70*, 2620.
(4) Mandel, M.; Leyte, J. C.; Stadhouder, M. G. *J. Phys. Chem.* **1967**, *71*, 603.

(5) Michaeli, I. *J. Polym. Sci., Part C* **1968**, *16*, 4169.
(6) Crescenzi, V. *Adv. Polym. Sci.* **1968**, *5*, 358.
(7) Davenport, J. N.; Wright, P. V. *Polymer* **1980**, *21*, 287.
(8) Jortner, J.; Sololov, K. *J. Phys. Chem.* **1961**, *65*, 1633.
(9) Robinson, G. W. *J. Chem. Phys.* **1967**, *46*, 572.
(10) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", 2nd ed.; Butterworths: London, 1965.
(11) Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolyte Solutions", 3rd ed.; Reinhold: New York, 1958.
(12) Verwey, E. J. W.; Overbeek, J. Th. G. "Theory of Stability of Lyophobic Colloids"; Elsevier: Amsterdam, 1948.
(13) Muresan, I.; Zador, L. *Stud. Univ. Babes-Bolyai, Chem.* **1973**, *18*, 89.
(14) Zador, L.; Muresan, I. *Rev. Roum. Chim.* **1974**, *19*, 353.
(15) Zador, L.; Muresan, I. *Stud. Univ. Babes-Bolyai, Chem.* **1979**, *24*, 3.
(16) Zador, L.; Muresan, I. *Stud. Univ. Babes-Bolyai, Chem.* **1979**, *24*, 47.
(17) Muresan, I.; Zador, L. *Bul. Inst. Politeh. sect. 2* **1980**, *26*, 59.
(18) Elisassaf, J. *J. Appl. Polym. Sci.* **1963**, *7*, S9.
(19) Wojtczak, Z. *Rocz. Chem.* **1968**, *42*, 1319.
(20) Wojtczak, Z. *Rocz. Chem.* **1971**, *45*, 237.
(21) Wojtczak, Z. *Rocz. Chem.* **1973**, *47*, 1703.
(22) Rossini, F. D.; Wagman, D. D.; Evans, W. H.; Levine, S.; Jaffé, I. "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards, Washington, D.C., Circular 500, 1952.
(23) Slansky, C. M. *J. Am. Chem. Soc.* **1940**, *62*, 2430.
(24) Price, E. In "The Chemistry of Non-aqueous Solvents"; Lagowski, J. J., Ed.; Academic Press: New York, 1966; Vol. I, Chapter 2.
(25) Henstock, H. *J. Chem. Soc.* **1934**, 1340.
(26) Stephen, H.; Stephen, T., Eds. "Solubilities of Inorganic and Organic Compounds"; Pergamon Press: London, 1963.
(27) *Encycl. Polym. Sci. Technol.* **1969**, *10*, 781 ff.
(28) Khokhlov, A. R. *J. Phys. A.: Math. Gen.* **1980**, *13*, 979.
(29) de Gennes, P.-G., "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(30) de Gennes, P.-G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. (Orsay)* **1976**, *37*, 1461.
(31) Odijk, T. *Macromolecules* **1979**, *12*, 686.
(32) Mandel, M. *Eur. Polym. J.* **1983**, *19*, 911.
(33) Oosawa, F. "Polyelectrolytes"; Marcel Dekker: New York, 1971.

Equivalence of Scaling Exponents from Static and Dynamic Measurements

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ABSTRACT: New dynamic light scattering measurements of the translational diffusion coefficient of relatively monodisperse samples of polystyrene in toluene indicate that at sufficiently high molecular weight, the hydrodynamic radius is directly proportional to the radius of gyration at infinite dilution. This observation constitutes a demonstration of the equality of the static scaling exponent ν and the hydrodynamic scaling exponent ν_H. In order to show the equality of the two scaling exponents, it is necessary to (1) use molecules of sufficiently high molecular weight, (2) have an adequately good solvent, (3) assess the effect of polydispersity, and (4) limit the scattering from intramolecular motion.

Introduction

To date, reported measurements of the hydrodynamic radius R_H of isolated random-configurationed macromolecules in good solvents do not increase as quickly with molecular weight M as do the values of the radius of gyration $\langle S^2\rangle^{1/2}$; that is, the reported values of the hydrodynamic coefficient ν_H where $R_H \propto M^{\nu_H}$ are less than the static scaling exponent ν where $\langle S^2\rangle^{1/2} \propto M^{\nu}$.[1] Several authors have argued that this is a consequence of the hydrodynamic radius being more heavily weighted by short-chain segments which are distributed more compactly than the farther separated segments that are more prominent in the averaging of the radius of gyration.[2,3] This argument implies that macromolecules of much higher molecular weight must be used for hydrodynamic measurements to reach the asymptotic scaling limit where $\nu_H = \nu$. Here we present dynamic light scattering measurements of the translational diffusion coefficient of polystyrene in toluene indicating that this asymptotic limit is obtainable with commercially available samples. It is the lack of hydrodynamic data on sufficiently high molecular weight material with carefully controlled polydispersity at sufficiently low scattering vector that has obscured the experimental verification of the equivalence of ν and ν_H.

Methods and Materials

Five relatively monodisperse polystyrene standards with a molecular weight in the range $(1\text{–}20) \times 10^6$ produced and partially characterized by Toyo Soda Manufacturing Co. were obtained from Varian. The samples were dissolved in toluene with index of refraction $n = 1.491$, distilled in glass by Burdick and Jackson Laboratories. Dynamic light scattering measurements were made in a Chromatix KMX-6DC low-angle laser scattering photometer with radiation of a wavelength $\lambda = 6.328 \times 10^{-5}$ cm at an angle $\theta = 4.02°$ from the transmitted beam. The individual photons were analyzed in a 48-channel Malvern K7023 autocorrelator in the single-clipped mode. The experiment was performed at 23 °C.

Each sample was measured at five roughly equally spaced concentrations below $c^*/2$, where

$$c^* = 2.5[\eta]^{-1} \approx M/N_{Av}\langle S^2\rangle^{3/2} \qquad (1)$$

is a concentration at which overlap of adjacent molecules becomes significant, $[\eta]$ indicates intrinsic viscosity, and N_{Av} is Avogadro's number. Solution concentrations are reported as a solute mass per solution volume of solution as in previous studies.[4] Samples were filtered into the scattering cell through a Millipore filter that had a pore size at least 6 times larger than the radius of gyration that Toyo Soda reported for the polymer in benzene at 30 °C.

Typically, 10^5–10^6 correlation functions over 2.5 decay periods were collected in the homodyne mode. The data were fit through the second cumulant with a variable base line.[5] A sample was

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