Titration of Poly(acrylic acid) and Poly(methacrylic acid) in Methanol

Herbert Morawetz* and Yongcai Wang

Department of Chemistry, Polytechnic University, Brooklyn, New York 11201.
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ABSTRACT: The dependence of the dissociation constant of poly(acrylic acid) and poly(methacrylic acid) on their degree of neutralization with lithium methoxide in methanol solution was determined by potentiometry and an indicator method. Poly(methacrylic acid) was found to be a significantly weaker acid. Viscosity measurements showed that the chain molecules of both polymeric acids expand at low charge densities but collapse at relatively low degrees of ionization. This collapse is not reflected in the titration curves.

Introduction

The titration behavior of poly(carboxylic acids) may be represented by

$$\mathrm{pH} = \mathrm{p}K_0 + \log[\alpha/(1-\alpha)] + \Delta G^{\mathrm{i}}_{\mathrm{el}}/kT = \mathrm{p}K_{\mathrm{p}}(\alpha) + \log[\alpha/(1-\alpha)] \quad (1)$$

where $\mathrm{p}K_0$ refers to an analogous monocarboxylic acid, α is the fraction of ionized carboxyls, $\Delta G^{\mathrm{i}}_{\mathrm{el}}$ is the electrostatic free energy required to remove a hydrogen ion from the charged polyion, and $\mathrm{p}K_{\mathrm{p}}(\alpha)$ is the apparent ionization constant of the polymer at a degree of ionization α. With aqueous poly(acrylic acid) (PAA), $\Delta G^{\mathrm{i}}_{\mathrm{el}}$ increases smoothly with increasing α, but with poly(methacrylic acid) (PMA), $\Delta G^{\mathrm{i}}_{\mathrm{el}}$ first increases and then remains constant over a range of α before rising again. This contrasting behavior of the two poly(carboxylic acids), first pointed out by Arnold,[1] was later interpreted by Leyte and Mandel[2] as reflecting a cooperative transition in PMA from a compact to an expanded form. Anufrieva et al.[3] reported that the resistance to chain expansion was eliminated when methanol was added to an aqueous PMA solution and concluded that the resistance to PMA expansion in water solution is due to hydrophobic bonding. Crescenzi et al.[4] carried out a calorimetric study of the ionization of PAA and PMA and found that while the enthalpy of ionization, ΔH^{i}, was a smooth function of α for PAA, the plot for PMA exhibited an endothermic peak (which became larger at higher temperatures) in the region in which viscometry and potentiometric titration indicated the transition from the contracted to the expanded form. Although the dissociation of hydrophobic bonds would be expected to be exothermic, Crescenzi et al. argued that the positive $\partial\Delta H/\partial T$ in the transition range pointed to hydrophobic bonds as responsible for the stabilization of the compact form of PMA. On the other hand, two arguments have been advanced against this interpretation: In the initial stages of PMA titration in 40% methanol, a medium in which no hydrophobic bonding would be expected, the UV absorption changes well beyond that expected from the ionization of carboxyls—an effect that is absent in the titration of PAA.[5] Also, in partially esterified PMA, the transition was seen at the same charge density as in unmodified PMA, although the ester groups should have strengthened hydrophobic bonding.[6]

Two years ago, a study of the potentiometric titration and viscometric behavior of PAA in methanol was reported from Mandel's laboratory.[7] It was found that the change with the degree of ionization of both the $\mathrm{p}K_{\mathrm{p}}$ and the reduced viscosity was strikingly different depending on whether $\mathrm{LiOCH_3}$ or $\mathrm{NaOCH_3}$ was used as titrant. Both produced a collapse of the polyion at a relatively low degree of neutralization, but this collapse was much sharper in the case of $\mathrm{NaOCH_3}$, leading to more compact particles. No analogous study of PMA in methanol seems to have been reported.

Results and Discussion

Since the pH determined in a potentiometric titration of a methanol solution is somewhat ambiguous, we expressed our data in terms of $\Delta\mathrm{p}K = \mathrm{p}K_{\mathrm{p}} - \mathrm{p}K_{\mathrm{Ac}}$, where $\mathrm{p}K_{\mathrm{Ac}}$ is the apparent pK of acetic acid in methanol. In titrating PAA and PMA with lithium methoxide, we determined $\Delta\mathrm{p}K$ either from potentiometric data or from the UV absorption of two indicators, *p*-nitrophenol and β-naphthol. The basic forms of these indicators have absorption maxima at 395 and 364 nm, respectively, and the absorption at these wavelengths may be used to determine their degree of ionization.

For any solution containing two acids, 1 and 2

$$\mathrm{p}K_1 + \log[\alpha_1/(1-\alpha_1)] = \mathrm{p}K_2 + \log[\alpha_2/(1-\alpha_2)]$$

$$\Delta\mathrm{p}K = \mathrm{p}K_1 - \mathrm{p}K_2 = \log[\alpha_1/(1-\alpha_1)] - \log[\alpha_2/(1-\alpha_2)] \quad (2)$$

and using this relation we found $\Delta\mathrm{p}K = 1.79$ for *p*-nitrophenol relative to acetic acid and $\Delta\mathrm{p}K = 2.4$ for β-naphthol relative to *p*-nitrophenol. In titrating PAA and PMA, we used *p*-nitrophenol indicator except for PMA at $\alpha > 0.5$, where *p*-nitrophenol approached full ionization and β-naphthol yielded more reliable data.

Figure 1 shows plots of $\Delta\mathrm{p}K$ for PAA ($\bar{M}_{\mathrm{v}} = 2.9 \times 10^5$)[8] and PMA ($\bar{M}_{\mathrm{v}} = 2.3 \times 10^5$)[9] relative to acetic acid. It may be seen that the values obtained by the indicator method are systematically higher by 0.2–0.3 pK unit compared to those obtained by potentiometry. This discrepancy may be due to the effect of the polymeric acid on the activity coefficients of the acidic and basic forms of the indicator. Up to $\alpha = 0.5$, the pK is higher by about a unit for PMA; at higher α, the difference diminishes since $\Delta\mathrm{p}K$ for PMA passes through a maximum, while it keeps rising for PAA.

Viscometric data (Figure 2) show that both polymeric acids expand at low charge densities, but the solution viscosity of PAA decreases beyond $\alpha = 0.25$ to return to its value in acid solution, and for PMA an even sharper viscosity drop was observed beyond $\alpha = 0.1$. This observation is similar to that reported from Mandel's laboratory for PAA in methanol.[7]

In commenting on these results we make the following points:

(1) The relatively large difference in the acidity of PAA and PMA is surprising. For monocarboxylic acids, the ionization constant decreases only by a factor of 2 when the α-carbon is substituted by a methyl group.

(2) In Manning's theory[10] counterions "condense" on polyions when the charge density exceeds DkT/e, where D is the bulk dielectric constant and e is the electronic charge. With $D = 33$ for methanol, the critical charge

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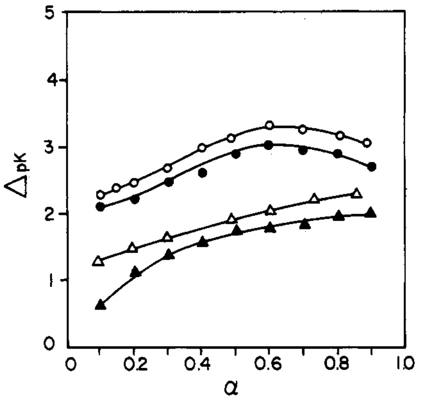

Figure 1. Dependence of ΔpK on the degree of neutralization α in methanol solution. Open points obtained by indicator method, full points by potentiometry. (○, ●) 0.0173 N PMA; (△, ▲) 0.0190 N PAA.

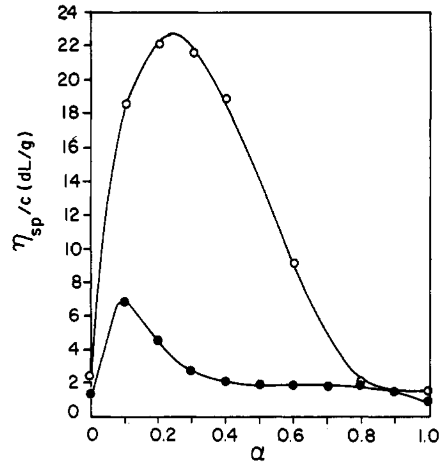

Figure 2. Dependence of the reduced viscosity of 0.0186 N PAA (○) and 0.0186 N PMA (●) in methanol on the degree of neutralization α at 26.3 °C.

density has a spacing of 17 Å between ionic charges, i.e., $\alpha = 0.15$, close to the value at which the chain expansions reached their maximum, although this point was significantly different for PAA and PMA. The collapse at higher α is similar to that reported at 10% ionization for poly(2-vinylpyridine).[11] We believe that this phenomenon is caused by the attraction between ion pairs formed by the counterion condensation. Such ion-pair association, acting *between* neutralized lightly sulfonated polystyrene, has been suggested[12] as the cause of the high solution viscosity of such polymers.

(3) It is striking that the collapse of the PAA and PMA chains, revealed by the viscosity data, is not reflected in the ionization equilibria. This suggests that the ΔpK depends only on short-range interactions, which are presumably insensitive to the overall expansion of the chain molecule. The steady rise in the pK of PAA after the collapse of the chain seems to reflect a dependence of ΔG^{i}_{el} on the concentration of ion pairs in the vicinity of an ionized carboxyl.

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Registry No. PAA, 9003-01-4; PMA, 25087-26-7; $LiOCH_3$, 865-34-9.

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