Polyelectrolyte Titration: Theory and Experiment

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Titration of methacrylic acid / ethyl-acrylate copolymers is studied experimentally and theoretically. At low salt concentrations, this polyacid exhibits a plateau in the titration curve below the neutralization point. The plateau has been often attributed to a first-order phase transition associated with polymer conformational changes. We argue that the specific shape of titration curves of hydrophobic polyelectrolytes is due to electrostatics and does not necessarily require a conformation change of the polyelectrolyte chains. We calculate the free energy at the mean-field level and its first-order (one loop) correction using a loop expansion. The latter is dominated by Debye-Hückel-like charge-charge correlations as well as by correlations between dissociation sites along the polymer chain. We show that the one-loop corrections to the free energy lead to titration curves that agree with experiments. In particular, the model explains the decrease of the pH at the plateau when the polymer concentration is increased or when salt is added to the solution.

I. INTRODUCTION

In recent years the search for environment-friendly materials has promoted the development of numerous water-soluble polymer applications. Polymers can be made water soluble by making them compatible with the strong polar environment of the aqueous media, e.g., by introducing either charges or strong dipoles on the chains \[\boxed{\text{1} \text{1}}\].

Most charged polymers (polyelectrolytes) have a hydrophobic backbone. This hydrophobicity induces an effective attraction between monomers which competes with the Coulomb repulsion between charges. As a result, hydrophobic polyelectrolytes exhibit complex behavior including conformation changes, macro- and meso-phase separation, self-association and aggregation \[\boxed{\text{1} \text{1}}\].

In spite of considerable theoretical and experimental effort, many questions remain open. In particular, the role of the coupling between hydrophobic attractions and long range Coulomb interactions on the physico-chemical properties of polyelectrolyte solutions is not fully understood. In this paper, we consider the role of such coupling in solutions of weak polyacids.

Weak acid monomers (denoted HA) can undergo dissociation of the type

\[
\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-
\]

where \(\text{A}^-\) is the charged monomer attached to the backbone, while the dissociated \(\text{H}^+\) charge dissolves into the solution. The dissociation/association is an equilibrium process satisfying detailed balance. The ionization degree determines the effective amount of charge on the polyelectrolyte chain, and it depends on the pH of the solution. At low pH the polymer is weakly charged while at high pH a larger fraction of monomers is dissociated and the polymer charge saturates to its maximal value. The most visible consequence is the solubility in water: hydrophobic polyacids can become water soluble at high enough pH, where the polymer charge is strong enough to overcome the chain hydrophobicity. In contrast to low molecular weight acids, the charged groups of polyacids are correlated as they are linked together along the chain. Indeed, the dissociation of one acid group is correlated in a complex way to the position and number of other charged groups on the chain. As a result, when the amount of charge on the chain...
varies, the chain conformation is affected, and in turn, influences the dissociation of other groups \[4,5,7,8\]. Studies of the interplay of these competing effects has attracted a large amount of experimental \[9–11\] and theoretical \[12–14\] interest. Additional motivation for these efforts is related to the use of water-soluble polyelectrolytes and in particular alkali-swellable polymers in many industrial applications, such as coatings, food and cosmetic industries \[15,16\].

An elementary and widespread experimental tool to characterize polyacids is to perform titration experiments. In these experiments, a strong base like NaOH is added to a solution of weakly charged polyelectrolytes. The pH of the solution and the equilibrium dissociation depends not only the amount of added base (like for ordinary acids \[19\]), but also on the polyelectrolyte concentration and presence of salt \[17,18\]. The overall shape of the titration curve depends on the nature of the polyelectrolyte which is titrated \[17\]. In the case of poly(acrylic) acid, the pH increases steadily with the dissociation degree. In contrast, the titration curve of poly(methacrylic) acid shows a maximum at low dissociation. Such a non-monotonous dependence has been related to a conformational transition. The case of hydrophobic polyelectrolytes is still more intriguing: the titration curve shows a large plateau where the pH is almost constant before the neutralization point is obtained. It has been argued in the literature that this plateau could be associated with a first-order phase transition between collapsed and swollen states of the polyacid chains \[7,20\].

In this paper we show that this peculiar shape of the titration curves can be explained without the need to rely on conformational phase transition of the polyacid chains. By including the effect of correlations of charges along the chains in the free energy, titration curves are calculated and show a behavior similar to the curves obtained in experiments. In particular, we explain how the pH depends on the polymer concentration and the amount of added salt. This dependence is special to polyacid solutions and is much weaker in monomeric acid solutions.

The paper is structured in the following way: in the next section the mean-field free energy, its one-loop correction and the resulting titration equations and curves are presented. Then, the experimental measurements of the titration of methacrylic acid / ethyl-acrylate copolymers (MAA-EA) are discussed in Sec. III, and the comparison between theory and experiment is presented in Sec. IV. The full formalism relying on a field theoretical approach will be presented in a forthcoming publication.

**II. THEORY**

We present first the free energy leading to titration curves of weak polyacids in presence of added salt. Our system consists of four dissociating species: water, methacrylic acid monomers (denoted HA), NaOH titrating base and NaCl salt. The dissociation reactions are written as:

\[
\begin{align*}
H_2O & \rightleftharpoons H^+ + \text{OH}^- , \\
HA & \rightleftharpoons H^+ + \text{A}^- , \\
\text{NaOH} & \rightarrow \text{Na}^+ + \text{OH}^- , \\
\text{NaCl} & \rightarrow \text{Na}^+ + \text{Cl}^- .
\end{align*}
\]

The partial dissociation of water and acid monomers is accompanied by an energy cost of breaking the molecular bond. They are denoted as \(\Delta_1\) and \(\Delta_2\), respectively (in units of the thermal energy \(k_B T\)), and they are related to the mass action law \[13\] as will be detailed below. Since NaOH is a strong base it is fully dissociated. Similarly, the salt is fully dissociated.

The polymer used in the experiment is a statistical copolymer composed randomly of two monomers: methacrylic acid and ethyl-acrylate. The total polymerization index is denoted as \(N\). A fraction \(f = 1/3\) of the monomers are composed of the methacrylic acid, i.e. they are ionizable. Since the charged monomers are distributed uniformly along the chain, we assign a partial charge \(f_e\) to each monomer ("smearing" the charges along the chain). Note that \(f_e\) is the nominal charge of each monomer, while the actual charge is related to the partial dissociation of the acid monomers.

The concentration of monomers in the solution is denoted \(c_m\) while the concentrations of the small ions are denoted \(c_{\text{H}}\), \(c_{\text{OH}}\), \(c_{\text{Na}}\), \(c_{\text{Cl}}\).

The base concentration added to the solution is denoted \(c_B\) and its ratio to the MAA monomer concentration is defined as the degree of neutralization \(\gamma\)

\[
\gamma \equiv \frac{c_B}{fc_m}
\]

where \(\gamma\) varies between zero (no added base) and infinity (large base excess). It is also useful to define the degree of ionization \(\alpha\) of the acid
\[ \alpha = \frac{[A^-]}{[HA] + [A^-]} = \frac{[A^-]}{f_{cm}} \]  

where \([A^-]\) and \([HA]\) are the concentrations of dissociated and non-dissociated monomers, respectively. This degree of ionization is related to the pH via

\[ \text{pH} = \text{pK}_A + \log_{10} \frac{\alpha}{1-\alpha} \]  

In addition, due to charge neutrality, \(\alpha\) and \(\gamma\) are related via

\[ \alpha = \gamma + \frac{[H^+] - [OH^-]}{f_{cm}} \]  

The conservation of mass implies the following relation between the ion concentrations:

\[ c_{Na} = c_B + c_{Cl} \]

Note that the Cl\(^-\) ions come only from the salt, while the Na\(^+\) come both from the base and the salt. Similarly, the OH\(^-\) ions come from the dissociation of water and base, whereas the H\(^+\) ions come from the dissociation of water and monomeric acid.

**A. Free energy**

We denote the full free energy as \(F = F_0 + \Delta F\), where \(F_0\) is the mean field term and \(\Delta F\) is the one-loop correction. Below we discuss the two terms of the free energy separately.

1. **Mean-field free energy**

In a separate work, the mean-field free energy (per unit volume and in units of \(k_B T\)) is shown to be

\[ \beta F_0 = \frac{c_m}{N} (\log c_m w_m - 1) + \sum_{j=H,OH,Na,Cl} c_j (\log c_j w_j - 1) - \frac{v}{2} \frac{c_m^2}{c_m^2} + \frac{w}{6} \frac{c_m^3}{c_m^3} - \lambda_0 c_m \]

\[ - (c_{OH} - c_B) \Delta_1 - (c_H + c_B - c_{OH}) \Delta_2 + (c_H + c_B - c_{OH}) \beta e \varphi_0 - f_{cm} \log(1 + e^{\beta e \varphi_0}) \]  

The following two terms represent the energy cost of dissociation of water molecules and acid monomers. We define by \(\Delta_1\) the energy loss for each dissociation of a water molecule

\[ H_2O \rightleftharpoons H^+ + OH^- \]

and by \(\Delta_2\) the energy loss for each dissociation of an acid molecule

\[ HA \rightleftharpoons H^+ + A^- \]

The number of OH\(^-\) ions coming from dissociation of water molecules is equal to the difference between the total number of OH\(^-\) ions and those coming from the NaOH base. Similarly, the number of dissociated acid groups is equal to the difference between the total number of H\(^+\) ions and the number of H\(^+\) ions coming from the water.

Finally, the last two terms account for the electrostatic energy, \(\varphi_0\) being the electrostatic potential in the solution. The first one is the electrostatic energy of the small ions, while the second is the electrostatic free energy of partially dissociated monomers \([21]\).
2. One-loop correction to the free energy

The one-loop correction to the mean-field free energy $\Delta F$ will be presented in detail in a forthcoming publication. It is obtained by integrating over the quadratic fluctuations of the concentration fields. The correction term to the free energy is given (up to an additive constant) by

$$\beta \Delta F = \frac{1}{2} \int \frac{d^3 q}{(2 \pi)^3} \log \Sigma(q)$$

$$\Sigma(q) = \left[ 1 + (\omega c_m - v)c_m N D(\eta) \right] (q^2 + \kappa^2) + 4 \pi l_B^2 A^2 N D(\eta)c_m$$

where the Debye-Hückel screening length $\kappa^{-1}$ depends on the total concentration of small ions $c_I$ and the effective charge of the chain $fA(1 - A)c_m$

$$\kappa^2 = 4 \pi l_B (c_I + fA(1 - A)c_m) \equiv 4 \pi l_B c_{\text{eff}}$$

$$c_I = c_{\text{H}} + c_{\text{OH}} + c_{\text{B}} + 2c_{\text{Cl}}$$

$$l_B = e^2/\varepsilon k_B T \approx 7 \text{ A}$$

is the Bjerrum length. The dissociation fraction of the acid monomers is given by

$$A = e^{\beta e \phi_0} / (1 + e^{\beta e \phi_0})$$

The Debye function $D(\eta)$ entering eq. (7) is given by

$$D(\eta) = \frac{2}{\eta} (1 + \frac{e^{-\eta} - 1}{\eta})$$

In addition to the small ion contribution to the electrostatic screening, eq. (8) includes a term proportional to $A(1 - A)$, where $A$ is defined in eq. (11) above. This term accounts for changes in the dissociation degree of monomers depending on the local electrostatic potential. At small $A$ values, $A(1 - A) \approx A$, and the polymer contribution is the same as that of disconnected monomers. However, as $A \to 1$ there is a substantial reduction (by the factor $1 - A$) of the effective polymer charge that contributes to screening [8,21]. This reduction can be understood in terms of charge correlation along the chain. Dissociated monomers prevent further dissociation of other monomers.

In our model, the concentrations $c_{\text{Na}}, c_{\text{Cl}}$ and $c_m$ are fixed by the amount of NaCl salt, NaOH base and polymer in the solution while the concentrations of dissociated $\text{H}^+$ and $\text{OH}^-$ ions depend on the degree of dissociation of water molecules and acid monomers (through the electrostatic potential $\phi_0$). Thus $c_{\text{H}}, c_{\text{OH}}$ and $\phi_0$ are variational parameters, determined by the requirement that the free energy $F = F_0 + \Delta F$ is an extremum. In titration experiments $c_{\text{H}}$ can be monitored directly through the pH of the solution.

3. Simplified free energy

In order to better understand the main contributions to the correction $\Delta F$ let us return to the expression for $\Sigma(q)$, eq. (8). First, we note that the Debye function is bound between 0 and 1 (see also eq. (27)). For typical values of the physical parameters (see also Sec. IV),

$$v \simeq 25 \text{A}^3 \quad w \simeq 100 \text{A}^6 \quad N \simeq 10^4 \quad c_m \simeq 1 \text{mM}$$

it is easily seen that for long chains ($N \gg 1$), the Debye function can be approximated by $N D(\eta) \simeq 12/a^2 q^2$, and

$$|\omega c_m - v|c_m N D(\eta) \ll 1$$

Thus, the effect of the solvent is small and will be neglected in this section

$$\Delta F \simeq \frac{1}{2} \int \frac{d^3 q}{(2 \pi)^3} \log \left[ q^2 + \kappa^2 + z \right]$$

(15)
where
\[ z = 4\pi l_B f^2 A^2 N D(\eta) c_m \] (16)

For the same range of parameters \( \kappa^2 \gg z \) and \( \Delta F \) can be expanded to first order in \( z \), \( \Delta F = \Delta F_0 + \Delta F_1 \):
\[ \Delta F_0 = \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \log \left[ q^2 + \kappa^2 \right] \] (17)
The integral can be calculated by including a cut-off at large \( q \), which cancels out the Coulomb self-energy, yielding
\[ \Delta F_0 = -\frac{\kappa^3}{12\pi} \] (18)

This result is the well known Debye-Hückel correlation energy of an electrolyte, because the polymer contribution is negligible and does not appear in this leading term. The correction \( \Delta F_1 \) is given by
\[ \Delta F_1 \approx \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \frac{z}{q^2 + \kappa^2} \approx 6f^2 A^2 l_B^{-1} \frac{\kappa}{\sigma^2} c_m \] (19)

This correction is due to correlations along the chain between dissociated monomers as can be seen from the following simple argument. Consider the screened electrostatic interaction between charged monomers on a single infinite chain. For a specific chain configuration the Coulomb energy per monomer is
\[ U_{el} = \sum_{j \neq 0} \frac{f^2 A^2 e^2}{\epsilon |r_j|} e^{-\kappa r_j} \] (20)
where \( r_j \) is the spatial distance between the \( j = 0 \) monomer and another \( j = \pm 1, \pm 2, \ldots \) monomer. For a Gaussian random walk, the typical (most probable) distance between monomers is given by
\[ \langle r_j \rangle = \left( \frac{2j}{3} \right)^{1/2} a \] (21)
Assuming that \( r_j \) can be approximated by \( \langle r_j \rangle \) in eq. (20), and \( \kappa a \ll 1 \), the sum over \( j \) can be replaced by a continuous integral leading to eq. (19).

B. Titration equations

The free energy depends on the species concentrations: \( c_{OH}, c_{Na}, c_{H}, c_m, c_{Cl} \). However, the concentration of monomers, \( Na^+ \) and \( Cl^- \), is fixed by the amount of polymer, base and salt added to the solution. On the other hand, the concentration of \( H^+ \) and \( OH^- \) ions is determined self-consistently by minimizing the full one-loop free energy \( F = F_0 + \Delta F \), eqs. (5), (6), with respect to \( c_H, c_{OH} \) and \( \varphi_0 \). The resulting equations of state determine the dependence of the pH of the solution on the other system parameters.

\[
\log(c_H \omega_H) + \beta e \varphi_0 - \beta \Delta_2 + 2\pi l_B I_1 = 0
\] (22)
\[
\log(c_{OH} \omega_{OH}) - \beta e \varphi_0 - \beta \Delta_1 + \beta \Delta_2 + 2\pi l_B I_1 = 0
\] (23)
\[
c_H + c_B - c_{OH} - f c_m A \left( 1 - 2\pi l_B (1 - A) (1 - 2A) I_1 + 2 AN f I_2 \right) = 0
\] (24)

where the quantities \( I_1 \) and \( I_2 \) are defined as:
\[ I_1 = \int_0^\Lambda \frac{k^2 dk}{2\pi^2} \frac{1 + N c_m (w c_m - v) D(\eta)}{\Sigma(k)} \] (25)
\[ I_2 = \int_0^\Lambda \frac{k^2 dk}{2\pi^2} \frac{D(\eta)}{\Sigma(k)} \] (26)

and \( \Lambda \) is a short distance (large \( q \)) cut-off.
With the full expression (12) of the Debye function $D(\eta)$, the integrals in (25), (26) cannot be performed analytically. However, for the values of the parameters used in the experiments, namely polymerization index $N \sim 10^4 - 10^5$ and monomer length $a \sim 5\text{A}$, it is possible to use a simplified form for the Debye function:

$$D(\eta) \simeq \frac{1}{1 + \eta/2}$$

(27)

As can easily be seen by comparing eq. (27) with the exact expression (12), the above form has the right behavior both at small and large values of $\eta$. Within this approximation, the integrals are given by:

$$I_1 = -\frac{1}{2\pi R^2} \frac{R^2 \kappa_+^2 \kappa_- / 2 + (\lambda + 1) \kappa^2 + u}{\kappa_+ \kappa_- (\kappa_+ + \kappa_-)}$$

(28)

$$I_2 = \frac{1}{2\pi R^2 (\kappa_+ + \kappa_-)}$$

(29)

where we have used the notation:

$$\lambda = Nc_m(wc_m - v)$$

(30)

$$u = 4\pi l_B A^2 N f^2 c_m$$

(31)

$$R^2 = Na^2 / 6$$

(32)

and

$$\kappa_+^2 = \frac{1}{R^2} \left( \lambda + 1 + \frac{R^2}{2} \kappa^2 \pm \sqrt{(\lambda + 1 - R^2 \kappa^2 / 2)^2 - 2u R^2} \right)$$

(33)

Note that in eq. (28) we have omitted a term, equal to $\Lambda / 2\pi^2$, which exactly cancels the Coulomb self-energy.

With these definitions, eqs. (22) and (23) can be recast in the form:

$$c_H \cdot c_{OH} = 10^{-14} e^{-4\pi l_B I_1}$$

(34)

which shows the change induced by fluctuations on the water dissociation constant and

$$c_H = 1 - \frac{A}{A e^{-2\pi l_B I_1}}$$

(35)

These two equations, together with eq. (24), which expresses charge neutrality at the one-loop level, are solved iteratively. The numerical solution is obtained by using the mean field values as a starting point for the iterations, and convergence is usually achieved after a few iterations.

C. Structure Function — $S(q)$

In scattering experiments the structure function $S(q)$ is readily obtained. It is related to the Fourier transform of the various density-density correlations in the sample. For example, we can regard the monomer-monomer correlations:

$$S(q) = \frac{\langle \delta c_m(q) \delta c_m(q) \rangle}{c_m}$$

(36)

Since the one-loop expansion takes into account Gaussian fluctuations, it can also be used to calculate the structure function. The result is

$$S^{-1}(q) = \frac{1}{ND(\eta)} + wc_m^2 - wc_m + \frac{f^2 A^2 4\pi l_B c_m}{q^2 + \kappa^2}$$

(37)

The inverse structure function $S^{-1}(q)$ is the energy penalty associated with density fluctuations at a wavenumber $q$. A minimum in $S^{-1}(q)$ corresponds to the strongest fluctuating wavenumber $q^*$. As a result, incoming radiation at this wavenumber interacts most strongly with the sample and a peak appears in the structure function and consequently in the scattering intensity.

An instability appears when $S^{-1}(q)$ vanishes, corresponding to a divergence of the peak in the structure function. When the instability appears at a finite $q = q^*$ the system undergoes a meso-phase separation and becomes spatially modulated. If, however, the instability is at $q = 0$ the system undergoes a macrophase separation. In our case this occurs when

$$wc_m = wc_m^2 + \frac{1}{N} + \frac{f^2 A^2 c_m}{c_{\text{eff}}}$$

(38)

Recall that $c_{\text{eff}}$ and $A$ depend on the pH and the degree of neutralization.
III. EXPERIMENT

A. Preparation of samples

The copolymer polyelectrolyte chains used in this study are prepared by standard emulsion polymerization techniques using neutral ethyl-acrylate (EA) monomers and methacrylic acid (MAA) monomers. The methacrylic acid is a weak acid with $pK_A = 4.5$. The weight fraction of MAA in the copolymer is equal to 0.35 taken to be $f = 1/3$ in the theoretical section. The emulsion polymerization is performed under starved monomer conditions. Under these conditions, the MAA and EA monomers are evenly distributed along the polymer chain. From size exclusion chromatography, we have estimated the molecular weight of the chains to be of the order of 106 daltons, corresponding to a polymerization index $N \approx 10^4$. The MAA-EA copolymers precipitate from the aqueous solution, as they are insoluble in water. The precipitate is carefully washed by ultrafiltration in order to remove surfactants, unreacted monomers and initiators. This cleaning procedure is stopped when the resistivity of the water flushed through the separation membrane is that of pure water (18.2 MΩ/m). The solid content of the stock solution is then determined accurately by drying and weighing.

B. Titration measurements

Polymer solutions at different weight concentrations are prepared by mixing weighted amounts of the stock solutions with de-ionized water. The dissolution of CO$_2$ is prevented by carefully de-gassing the solution with nitrogen. Each of the polyelectrolyte solutions is neutralized by an NaOH solution with a molar concentration ranging from 0.1M to 2M depending on the polymer concentration. Upon neutralization, the methacrylic acid is neutralized and repulsive forces due to the negative charges cause the chain to expand, resulting in the progressive solubilization of the polymer chains. As a result the solution becomes transparent and its viscosity increases. In the following, we shall characterize the neutralization of the polymer chains by the degree of neutralization, $\gamma = c_B/(f c_m)$, which is the ratio of the amount of added base to the amount of available acids groups. Titration experiments are performed using a pH-meter (Metrohm 691) with a combined glass electrode. The measurements are made at 20°C with constant stirring under a nitrogen atmosphere. In parallel, the conductivity of the solution is measured (Metrohm 712).

The measurements reveal that all small ions present in solution are free and contribute to the conductivity. This was checked at different $\gamma$ values by changing the polymer concentration. The measured conductivity is the exact sum of the conductivities coming from the Na$^+$ ions (whose concentration is known from the amount of added NaOH base), and H$^+$, OH$^-$ (known from the pH), while the small contribution of the polymer is negligible. These conductivity measurements demonstrate that the distribution of small ions is homogeneous in the solution, and no evidence for the Donnan effect and counter-ion condensation is observed.

IV. RESULTS: COMPARISON OF EXPERIMENTS WITH THEORY

In this section we present the experimental results for the titration curves of MAA-EA copolymers and compare them with the theory of Sec. II. Fig. 1(a) shows the titration curves measured for different polymer concentrations. They differ substantially from the titration curves of monomeric methacrylic acid (MAA). Methacrylic acid in aqueous solution has the typical behavior of a weak monomeric acid. The pH increases monotonously with $\gamma$, takes the value $pK_A = 4.5$ for $\gamma = 0.5$ and then jumps near $\gamma = 1$. By contrast, the titration curves of MAA-EA copolymers exhibit the following behavior: in the range $0 \lesssim \gamma \lesssim 0.2$, the pH increases sharply to a plateau value which remains nearly constant up to $\gamma \approx 1$ where the amount of added base equals that of the monomer (neutralization point). The jump of the pH for $\gamma \lesssim 0.2$ is associated with a swelling phase transition of the latex particles i.e. a change of conformation of the chains. A similar phenomenon has been observed during the titration of pure poly(methacrylic acid) [23].

Let us mention that it is possible to calculate the swelling transition of the polymer as function of monomer concentration, $c_m$. This can be done by minimizing the free energy with respect to $c_m$ (in addition to the other annealed degrees of freedom discussed above). Any non-convexity of the free energy signals the existence of a polymer precipitate in excess water.

On Fig. 1 several titration curves are plotted for different concentrations of the same MAA-EA copolymer. As the concentration $c_m$ increases, the jump in the pH at $\gamma \approx 1$ increases. Note that the deviation between the pH of the MAA monomeric acid and the MAA-EA copolymers ($c_m = 0.1$ M in Fig. 1), is large in the plateau region ($\gamma < 1$).
On the other hand, the deviation is quite small for \( \gamma > 1 \) when the acid is almost completely dissociated. The value of the pH at the plateau depends strongly on the polymer concentration: the larger the \( c_m \), the lower the plateau. It is surprising that even though MAA-EA copolymers contain carboxylic groups, the plateau value of the pH below \( \gamma = 1 \) may be neutral or even greater than 7.

This difference in behavior between the MAA monomers and MAA-EA copolymers might be associated with a complex structure of the MAA-EA copolymer for \( \gamma \lesssim 1 \). Collapsed microdomains may exist on the chains due to the competition between the hydrophobic attraction and Coulomb repulsion. The plateau region suggests the existence of such collapsed microdomains along the chains. For \( \gamma \gtrsim 1 \) the chains are in a swollen state and their behavior resembles that of monomeric weak acid.

In Fig. 1(b) we plot for comparison the titration curves as calculated from the theory. The titration equations presented in Sec. II.B are solved numerically by an iteration procedure starting from the mean field values as the first iteration and including the corrections of the second iteration. Since there are a couple of unknown physical parameters (like the second and third virial coefficients, \( v, w \) and the monomer size \( a \)), we do not try to fit the experimental titration curve. Rather, we note that the corresponding theoretical curves look very similar to the experimental ones, demonstrating the same type of plateau for low \( \gamma \) and the same trend with the monomer concentration.

Figure 2 shows the effect of adding a monovalent salt (NaCl). The overall shape of the titration curves remain unchanged. However, the value of the pH at the plateau increases upon the addition of salt, while the pH for \( \gamma \gtrsim 1 \) is essentially independent on the salt concentration. This indicates that neutralization of the carboxylic groups carried by the chains becomes easier as the ionic strength is increased. As the Coulomb interaction is screened by the salt, there is less correlation between charged groups along the chain when their distance is larger than the Debye length. Therefore, monomers separated by distances larger than the Debye length can dissociate independently from each other. For \( \gamma \gtrsim 1 \), almost all the charged groups on the chains are dissociated; thus, the salt has no effect on the pH. The comparison between experiment and theory is presented in part (a) and (b), where a good agreement can be observed. Note the large deviation from the experimental results for higher salt concentration (\( c_{\text{NaCl}} = 0.1 \text{ M} \)).

In Fig. 3, the plateau value of the pH is plotted on a semi-log plot as function of the ionic strength \( c_I = c_{\text{Na}} + c_{\text{H}} + c_{\text{Cl}} + c_{\text{OH}} \). The plateau value of the pH is taken at \( \gamma = 0.5 \). It is interesting to note that the different points taken at various salt and base concentrations collapse on a single curve. This result indicates that the pH is dominated by electrostatic effects and not by conformation changes of the chains. When the ionic strength increases, the fixed charges carried by the polymer are screened and the energy associated with the dissociation of a carboxylic group decreases.

This behavior can be characterized semi-quantitatively by noting that when \( \gamma \simeq 1/2 \) the pH is much higher than the pK\(_A\) and, therefore, \( \gamma^{(0)} \to 1 \) and \( A \to 1 \). Consequently, at the plateau \( \Delta \gamma \simeq 1/2 \). To first order in \( 10^{pK_A - \text{pH}} \) the plateau value can be obtained from the simplified free energy, Sec. II.A.3 and reads:

\[
pH_{\text{plateau}} \simeq pK_A + \log_{10} \left[ \kappa \left( \frac{10^{pK_A}}{a^2} \right) + f l \right]
\]

(39)

Recall that \( \kappa \) depends on the total amount of ions in the system through eq. (b). The above expression is used for the plot of the solid curve of Fig. 3b, where the pH of the plateau is shown as a function of the effective ionic strength \( c_{\text{eff}} \) defined in eq. (b). In this regime, the difference between \( c_{\text{eff}} \) and \( c_I \) is a small correction of order \( 10^{pK_A - \text{pH}} \).

Equation (39) exhibits three different regimes depending on the relative importance of the various contributions to the logarithmic term. In each regime, \( c_{\text{H}} \) has a different power law dependence on the total ionic strength \( c_{\text{eff}} = c_I + f A (1 - A)c_m \) leading to different slopes in Fig. 3. At low ionic strength the second term dominates and \( c_{\text{H}} \propto c_{\text{eff}}^{-3/2} \) (long dashed line in Fig. 3b). At intermediate ionic strength the last term dominates and \( c_{\text{H}} \propto c_{\text{eff}}^{-1/2} \) (short dashed line). Finally, at high ionic strength (beyond the experimentally accessible values) \( c_{\text{H}} \propto c_{\text{eff}}^{-1/2} \).

In Figure 4 the effect of polymer concentration and ionic strength on \( S(q) \) is shown. The structure function is calculated at the plateau regime were \( A \simeq 1 \). The dependence on the controlled system parameters: the pH, the salt concentration and the degree of neutralization \( \gamma \) is taken implicitly into account in \( c_{\text{eff}} \). At low values of \( c_{\text{eff}} \), the structure function exhibits a peak at finite \( q \) corresponding to the most favorable density–density fluctuations. As \( c_{\text{eff}} \) increases, \( S(q \to 0) \) increases until the peak disappears. This increase is accompanied by an increase in the osmotic compressibility of the solution.

The effect of varying the polymer concentration \( c_m \) at a fixed \( c_{\text{eff}} \) is depicted in the inset. The peak is stronger at lower polymer concentrations indicating that fluctuations become considerably stronger at lower concentrations. This effect agrees well with the titration curves shown in Fig. 1. Indeed, at low polymer concentrations the shift in the titration curve is stronger than at high concentrations. The peak position shifts to higher wavenumbers (smaller length
scale) at higher concentration, similar to the correlation length of polymer solutions that decreases with increasing polymer concentration.

V. CONCLUSIONS

We have presented an experimental study of the titration of weak polyacids by a strong base. Our experimental findings performed on solutions of MAA-EA copolymers, are supported by theoretical calculations, which show similar trends of the pH variation with the concentration of added base, salt and polyacid.

Titration experiments are one of the simplest and most useful experimental tools to probe the degree of neutralization of monomeric and polymeric acids. Since titration curves of weak acids are universal, any deviation from this behavior, as observed here, can be the signature of a complex behavior coupling Coulombic and hydrophobic interactions.

The most striking feature is the existence of a plateau of the pH for low degree of neutralization. The plateau in the pH is at higher value than the corresponding pH of the monomeric acid indicating that the charges on the chain inhibit the dissociation of other charged groups. The pH is not affected strongly by further addition of the base till the neutralization point $\gamma = 1$. This is probably due to the existence of collapsed microdomains along the chains for $\gamma \lesssim 1$. The pH at the plateau decreases as function of the ionic strength. This demonstrates that non-specific electrostatic interactions are responsible for the existence of the plateau, since the pH depends mostly on the amount of small ions and not on their type (for a fixed degree of neutralization).

The theory presented above includes one-loop corrections to the mean-field free energy. On the mean-field level, there is no difference between the polymeric and monomeric titration curves except for the translational entropy of the chains. The one-loop correction couples the chain connectivity with the electrostatics and induces the large deviations in the titration curves. We modeled the polyacid as flexible chains using the standard Debye function. Our formalism can also be applied to different models of chain elasticity. In particular, for the case of semi-flexible chains the same titration equations are obtained with a modified Debye function taking into account the persistence length of the chains.

Finally, it will be interesting to complement this study by scattering experiments where it might be possible to resolve the chain microstructures and relate them to the degree of ionization of the chains.

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Fig. 1  pH plotted as a function of the degree of neutralization $\gamma$ with no added salt. In (a) the experimental titration curves are shown for different polymer concentration: $c_m = 1 \text{mM (10}^{-4} \text{ g/g)}$ full circles; $c_m = 10 \text{mM (10}^{-3} \text{ g/g)}$ full triangles; $c_m = 0.1 \text{ M (10}^{-2} \text{ g/g)}$ full squares. The open circles denote the titration curve of the monomeric MAA at $c_m = 0.1 \text{ M (10}^{-2} \text{ g/g)}$. In (b) the theoretical results are plotted for the same polymer concentrations: $c_m = 1 \text{ mM (dotted curve)}$; $c_m = 10 \text{ mM (short dashes)}$; $c_m = 0.1 \text{ M (long dashes)}$. The solid line corresponds to the mean field solution (no correlations and no connectivity) for $c_m = 0.1 \text{ M}$. It reproduces nicely the conventional monomeric titration curve. The polymer parameters we take are: $a = 5 \text{ Å}, f = 1/3$ and $\text{pK}_A = 4.5$.

Fig. 2  pH plotted as a function of the degree of neutralization $\gamma$ for different amount of added salt. The experimental values in (a) are compared with the theoretical ones in (b). The polymer concentration is $c_m = 1 \text{ mM (10}^{-4} \text{ g/g)}$. The concentration of NaCl in the solution is: $c_{\text{NaCl}} = 0$ (open circles/solid line), 1 mM (full circles/dotted curve), 10 mM (full diamonds/short dashes), 0.1 M (full squares/long dashes). The theoretical curves are calculated using the same parameters as in Fig. 1.

Fig. 3  Semi-log plot of the pH at the plateau as a function of the ionic strength. Comparison between experimental results (a) and theoretical calculation (b). The experimental measurements are plotted in (a) as function of the total amount of small ions $c_I$. The open circles give the pH of salt-free solutions at different monomer concentration extracted from Fig. 1. The full symbols give the pH of solutions with increasing amount of added salt: $c_m = 1 \text{ mM (10}^{-4} \text{ g/g)}$ full circles, and $c_m = 0.1 \text{ M (10}^{-2} \text{ g/g)}$ full triangles. The data collapse indicates that the pH depends only on the total ionic strength. The theoretical results are plotted in (b) as a function of $c_{\text{eff}} = c_I + fA(1 - A)c_m$ using the same parameters as in Fig. 1. See text for details of the approximations made in the calculation.

Fig. 4  The structure function $S(q)$ as function of the wavenumber $q$. The structure function is calculated at the plateau of the titration curve where $A \simeq 1$. The physical parameters used in the calculation are $a = 5 \text{ Å}, v = 25 \text{ Å}^3, w = 100 \text{ Å}^6, N = 10^4, f = 1/3$ and $\text{pK}_A = 4.5$. The monomer concentration is $c_m = 1 \text{ mM}$ while the effective ionic strength is $c_{\text{eff}} = 0.01 \text{ mM (solid line)}, c_{\text{eff}} = 1 \text{ mM (dotted curve)}$ and $c_{\text{eff}} = 0.1 \text{ M (dashed curve)}$. In the inset the effective ionic strength is fixed at $c_{\text{eff}} = 1 \text{ mM}$ while the polymer concentration is varied: $c_m = 1 \text{ mM (solid line)}, c_m = 10 \text{ mM (dotted curve)}$ and $c_m = 0.1 \text{ M (dashed curve)}$. 

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