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Letter

^{13}C Nuclear magnetic relaxation of tetraethylammonium cation in poly(acrylic acid) solution

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The condensation of tetraethylammonium cations on poly(acrylic acid) is a progressive process and its extent is limited; the discontinuity of the titration curve, when α approaches 0.40 ($\xi \approx 1$), is probably an indication of several polyion–counterion system internal changes.

The interactions between a polyelectrolyte and small ions in solution have been modeled by two major analytical theories: (1) Manning's counterion condensation (CC) model[1] and its later developments,[2–8] and (2) models using the Poisson–Boltzmann equation (PB model).[9–11] In the original CC model, Manning states that the "condensation" of counterions refers to a certain type of binding of counterions by a polyion of suitably high charge density. Counterion condensation occurs if the charge density parameter ξ exceeds unity (for monovalent counterions). As a result of condensation, the effective charge fraction on the polyion is reduced to $1/\xi$; thus $(1 - 1/\xi)$ counterions per polyion charge are bound, where ξ is given by

$$\xi = e^2/(\varepsilon kTb)$$

using SI units and standard symbols for physical constants. The parameter b is the (average) axial separation between the structural charges on the polyion. The PB model requires the solution of a nonlinear second-order differential equation for the electrostatic potential around the polyion. Commonly, it assumes that the polyion solution can be modeled using a cylindrical cell of radius R with the polyion at its centre (the PB cell model). The polyion is taken to be a rod that is infinitely long, with radius a and a uniform charge density. Solution of the PB equation for rodlike polyions must be carried out by interactive methods, since (with added salt present) there is no exact analytic expression for the potential.[12] The two theories provide different molecular pictures of the condensation phenomenon. A molecular level titration should reveal this process.[13]

A wide variety of physical methods have been employed to study counterion "binding" to polyions.[13] Among them, ^{23}Na NMR relaxation (T_1 and T_2)[11,14–18] measurements during titration provide much detailed information about the interaction of a charged polyion with counterions. However, the complications arising from solvation upon the Na^+ and other metal ion NMR relaxation in water have been questioned.[14,19] There are neither Na^+ or Li^+ NMR relaxation titration curves available, which disclose the critical onset of counterion condensation, nor directly indicate that the progressive process of counterion condensation stops at a critical neutralization point.

^{13}C Nuclear magnetic relaxation occurs mainly through the protons one bond away. In aqueous solution, a covalently bonded carbon atom is much less solvated than a charged sodium atom. In comparison to other nuclei, ^{13}C NMR relaxation can thus provide more reliable information, being less susceptible to solvation effects.[20]

Tetraalkylammonium cations, such as $(CH_3)_4N^+$, $(CH_3CH_2)_4N^+$ and $(CH_3CH_2CH_2CH_2)_4N^+$ have been used in studies of polyelectrolyte interaction with small counterions on a number of previous occasions, especially for $^{23}Na^+$ nuclear magnetic relaxation in DNA solution and for potentiometric titration of weak polyelectrolytes.[11,13,18] Except for the "binding" affinity, tetraalkylammonium cations behave in the same way as Na^+ in interacting with other polyelectrolytes. The study of counterion condensation by ^{13}C NMR relaxation was first reported at the 38th ENC.[21]

It has been found that ^{13}C nuclear magnetic relaxation T_1 of the tetraethylammonium cation (TEAC) in water has a linear or approximately linear concentration dependence in the range of about 0.1 to 1 M (Fig. 1).[21] When the concentration of TEAC in water increases from 0.1 to 1 M, the ^{13}C T_1 of $-CH_2-$ in the ethyl group decreases by about 500 ms and the ^{13}C T_1 of CH_3- in the ethyl group decreases by about 240 ms. It is known that the maximum counterion concentration on the polyelectrolyte surface could be as high as about 1 M. The change in ^{13}C T_1 of TEAC with concentration is sufficient for monitoring precisely the counterion concentration change on the polyelectrolyte surface by measuring the ^{13}C T_1. This phenomenon might be understood as being due to cation aggregation, which reduces the mobility of the cation in solution. The linear relationship (Fig. 1) indicates that there is no significant conformation change of TEAC in the studied concentration range.

Direct titrations of poly(acrylic acid) (PAA) with tetraethylammonium hydroxide were carried out following the method described by Leyte and his co-workers.[14] The PAA used (Aldrich) had an average RMM of 2000 (GPC). Elemental analysis showed it to contain 0.9% sodium, and the water

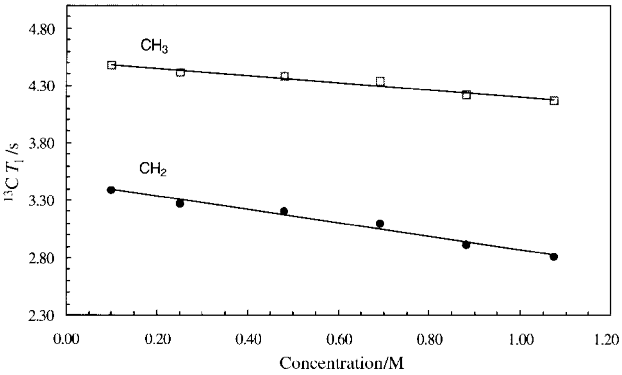

Fig. 1 ^{13}C T_1 of $(CH_3CH_2)_4NBr$ in 20% D_2O–80% H_2O at 30 °C as a function of its concentration. T_1 of $-CH_2-$: $R = 0.989$; T_1 of CH_3- : $R = 0.980$.

content was 2.1% (Karl–Fischer). The concentration of tetraethylammonium hydroxide from Fluka was determined by titration. Longitudinal relaxation times were measured on a Varian 400 MHz NMR spectrometer at 54.58 ppm for ^{13}C $-CH_2-$ and 9.26 ppm for ^{13}C CH_3- using the inversion recovery method provided by Varian VnmrX™ software. All experiments were performed at 30.0 ± 0.1 °C using the NMR spectrometer variable temperature control.

Fig. 2 shows the longitudinal relaxation times of ^{13}C ($-CH_2-$) and ^{13}C (CH_3-) in PAA solutions at various degrees (α) of neutralization. Both titration curves are "V" shaped and have a sharp slope discontinuity at $\alpha = 0.71$. The ^{13}C T_1 of the $-CH_2-$ titration curve can be separated into three sections.

In the first section ($0.12 < \alpha < 0.40$) the plot is a flat straight line. This means that the average mobility of TEAC in this system is almost the same at different α. Tetraethylammonium bromide was added to a 0.6 N PAA solution instead of tetraethylammonium hydroxide. The ^{13}C T_1 of $-CH_2-$ and CH_3- is 450 ms larger than that when tetraethylammonium hydroxide was used. (If comparing to the ^{13}C T_1 obtained in 0.3 N PAA titration solution when tetraethylammonium hydroxide was used, the ^{13}C T_1 of tetraethylammonium bromide measured in 0.6 N PAA solution is more than 250 ms larger.) This suggests that the TEAC is "binding" with PAA or condenses on the partially charged PAA surface even at this low charge density (when $\alpha < 0.35$, $\xi < 1$).[7] Because the concentration of TEAC on the PAA surface is too low to exhibit its ^{13}C T_1 concentration dependence, the plot is a flat straight line. The same titration has also been done in 0.6 N PAA solution. The plot is a flat straight line in the range of α from 0.09 to 0.40. Similar counterion condensation on polyions with $\xi < 1$ was also observed by Joshi and Kwak.[22]

In the second section ($0.40 < \alpha < 0.71$) of the plot, when α increases, ^{13}C T_1 decreases. The downward linear relationship between them indicates that all of the freshly added TEAC condenses on the PAA surface. The decrease of ^{13}C T_1 results from the increase of the TEAC concentration adsorbed on the charged surface.

In the last section ($\alpha > 0.71$) an upward linear plot (a positive linear relationship) is observed in which ^{13}C T_1 increases as α continues to increase. The linear plot suggests that TEAC no longer condenses on the PAA surface, although negative charge continues to be generated on the surface of PAA as base is added. All of the freshly added TEAC goes into solution as "free" TEAC. The ^{13}C T_1 is linearly enhanced by the freshly added "free" TEAC in solution. The titration curve thus shows its second "discontinuity". This means that only a limited amount of counterions can condense on the polyion or only a limited amount of charge on the polyion can be neutralized by counterions, meaning that the critical point should be at $\alpha = 0.71$[23] which is derived from Fig. 2 (see below). This part of the titration curve has been reproduced by adding TEAC bromide instead of TEAC hydroxide to the titration solution.

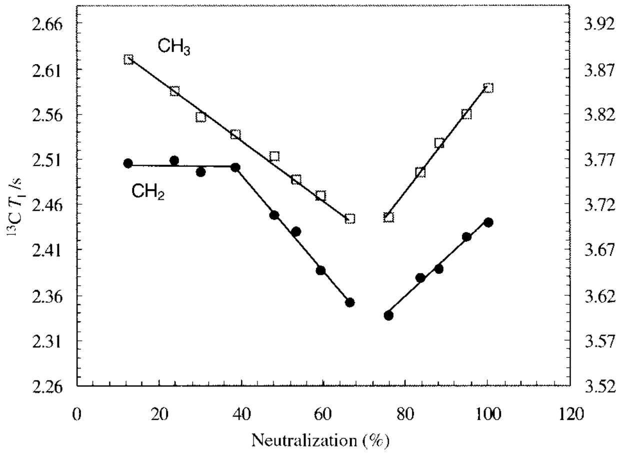

Fig. 2 ^{13}C T_1 of tetraethylammonium cation in 0.3 N poly(acrylic acid) aqueous solution at 30 °C as a function of the degree of neutralization α.

The same results can be derived from the titration curve obtained from plotting the ^{13}C T_1 of CH_3- *vs.* α. (Fig. 2) The only difference between the two titration curves is that the one CH_3- is linear for all values of $\alpha < 0.71$. There is no flat section in the region of $0.12 < \alpha < 0.40$. In comparison to $-CH_2-$, CH_3- is at the end of the ethyl chain and exhibits more freedom of movement. Therefore, the ^{13}C T_1 of CH_3- may be more sensitive to the concentration change at low α than that of $-CH_2-$. When $\alpha > 0.71$, the slope (0.585) of the plot for CH_3- is larger than the slope (0.425) of the plot for $-CH_2-$ because the ^{13}C T_1 of CH_3- is larger than that of $-CH_2-$ in TEAC. This further indicates that the increases in T_1 result from added TEAC, which remains "free" in solution. The same shape titration curves have been obtained in oligonucleotide aqueous solution. These results will be published separately.

The titration curve allows us to derive the critical α by extrapolating the second section and the last section towards each other. The intersection value of 0.71[23] agrees with the result (0.70) derived from an analysis of measurements of specific conductivity and the electrophoretic mobility of PAA at various extents of ionization α.[24,25] If we assume that the decrease in ^{13}C T_1 is mainly due to the increase in TEAC concentration on the poly(acrylic acid) surface, then the counterion (TEAC) concentration on the polyion can be estimated from Figs. 1 and 2. The result is 0.66 M, which is based on the titration curve of ^{13}C T_1 of $-CH_2-$. (If based on the titration curve of the ^{13}C T_1 of CH_3-, the result is 0.70 M.) It is generally believed that the associated counterion concentration on the polyion is in the range of 0.6–0.7 M.

These experimental results demonstrate that TEAC progressively condenses on poly(acrylic acid) with a build up of polyion charge, and the extent of the condensation is limited. When α approaches 0.40 ($\xi \approx 1$), the titration curve of $-CH_2-$ (^{13}C T_1) shows its first discontinuity in slope. This could be induced by polyion–counterion system internal changes, which include the start of the interaction between TEAC condensed on poly(acrylic acid), the change of charged poly(acrylic acid) conformation, and the birth of the counterion–polyion complex, as Manning has always emphasized.[6] The same sort of observations have been made by several researchers when the interaction between counterion and polyion at $\xi \approx 1$ was studied.[26] The titration curve of the ^{13}C T_1 of CH_3- *vs.* α does not show the slope discontinuity as α approaches 0.40. It may be that for CH_3-, being one more bond away from the charge centre, the ^{13}C T_1 is not sensitive to the polyion–counterion system internal changes at $\xi \approx 1$ as is the ^{13}C T_1 of $-CH_2-$. At $\alpha = 0.71$ ($\xi \approx 2$), both titration curves have a sharp discontinuity in slope. Obviously, the condensation of TEAC on poly(acrylic acid) has stopped even though the negative charge on the polyion continues to increase as TEAC hydroxide is added.[13,27–30]

In conclusion, the titration of the ^{13}C NMR relaxation T_1 of TEAC in poly(acrylic acid) solution provides a molecular picture of counterion condensation on a polyelectrolyte and the interaction between them. TEAC condensation on PAA is a progressive process and its extent is limited. The discontinuity of the titration curve, when α approaches 0.40 ($\xi \approx 1$), is probably an indication of several polyion-counterion system internal changes, such as the commencement of the interaction between TEAC condensed on poly(acrylic acid), the conformation change of charged poly(acrylic acid), and the start of counterion–polyion complex formation.

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29 One referee commented that "The sharp break at about $\alpha = 0.4$ in the $-CH_2-$ data is certainly persuasive of the abrupt beginning of some process at this stage of the titration. It probably indicates the beginning of binding, or condensation, of the TEAC. The author proposes that binding occurs even at the starting stages of the titration, and the break signifies a qualitative change in the mode, or effect, of binding. But the evidence for "early" binding is tenuous (weak). The change in relaxation time relative to TEA bromide solution is very small and could as easily be interpreted as the effect of viscosity differences. The interpretation as early binding is not essential to the strength of the paper, it rests on weak evidence." However, the idea of "early" binding is also based on the titration curve of ^{13}C T_1 of CH_3- *vs.* α. When $\alpha < 0.71$, the titration curve is a downward linear plot.

30 One referee noted that "The break at $\alpha = 0.7$ is interpreted as 'saturation' of TEAC binding, and the interpretation is reasonable in view of the evidence presented. Perhaps the binding saturates before complete neutralization because of the large size of the TEAC, which possibly prevents all of the neutralizing cation from clustering near the polymer surface."

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