Odd-even shell ionization of Astramol™ dendrimers

Abstract Potentiometric titrations of five generations of poly(propylene imine) dendrimers were performed at 0.1, 0.5, and 1.0 M KCl and NaCl. The titration curves reveal two-step protonation behavior similar to linear polyelectrolytes. The difference to linear polyelectrolytes is that the position of the intermediate plateau lies at 2/3 of the total ionizable groups. The intermediate plateau results from the stability of an onion-like structure where all odd shells of the dendrimer are protonated, while the even shells remain deprotonated. The titration curve features two distinct steps around pH 6 and 10. The Ising model permits a quantitative analysis of this protonation behavior.

Key words Dendrimer – potentiometric titration – Ising model

Introduction

The ultimate goal of studies on acid-base properties of polyelectrolytes is the prediction of the ionization behavior of arbitrary molecules from structural information. For linear polyelectrolytes, the linear chain Ising model turns out to be rather successful, and allows to rationalize acid–base properties of linear polyelectrolytes and their oligomeric analogs quantitatively [1–5].

The Ising model with nearest-neighbor interactions was recently extended to branched polyelectrolytes [6]. In contrast to linear molecules, experimental studies on the acid–base properties of a branched polyelectrolyte, where an ionized site has more than two charged neighbors, are scarce. To investigate the extended Ising model more thoroughly, further experimental data are needed.

In this paper we demonstrate that poly(propylene imine) dendrimers (recently introduced as Astramol™ dendrimers) are a system from which detailed information about the ionization of branched structures can be extracted.

Highly charged linear polyelectrolytes protonate in two steps. The intermediate plateau in the titration curve is related to a stable intermediate protonation state, where protonated and deprotonated groups alternate along the chain. This two-step behavior is caused by the short-range character of the interaction potential between ionizable sites. The splitting between the two protonation steps is related to the interaction energy of forming a pair of nearest-neighbor ionized sites.

As discussed below, two main differences between ionization behavior of dendrimers and the corresponding linear polyelectrolytes emerge [6]: (i) The intermediate plateau in the titration curve of a dendrimer arises at a degree of protonation 2/3, whereas for their linear analogues this occurs at half protonation. (ii) Since every dendrimer site has three nearest-neighbors, the overall effect of interactions is much stronger than for the linear polyelectrolyte with only two nearest-neighbors. In the latter case the splitting between the two protonation steps is therefore of the order of two times the splitting between the two protonation steps in a corresponding diprotic acid or base, whereas for the dendrimers this splitting is three times as large splitting.
Potentiometric titrations

The titration curves of five generations of 1,4-diaminobutane poly(propylene imine) dendrimers, obtained from DSM, the Netherlands, are shown in Fig. 1. A schematic picture of this sequence is represented on the right-hand side of Fig. 1, all structures emanating from a 1,4-diaminobutane core with propylene imine monomers. In the following these dendrimers will be abbreviated with DAB-dendr-(NH₂)ₓ, with x = 4, 8, 16, 32, and 64. Packing constraints with the outermost shells make the complete synthesis of higher generations difficult.

All potentiometric titrations were carried out at a temperature of 25 ± 1 °C, with HCl and carbonate-free NaOH/KOH. NaCl/KCl was used as the supporting electrolyte to keep the ionic strength constant at 0.1, 0.5 and 1.0 M during the experiment. The titration curves have an error of ±0.05 on the pH scale and an error of ±10⁻² in the degree of protonation. More detailed information about the experimental conditions and analysis methods is described in Ref. [7].

Fig. 1 Experimental titration curves of poly(propylene imine) dendrimers DAB-dendr-(NH₂)ₓ (schematic representations on right-hand side) plotted as the degree of protonation φ as a function of pH in KCl as background electrolyte. The ionic strengths are 0.1 M (▲), 0.5 M (■) and 1.0 M (●). The curves are translated along the ordinate for clarity. On the left-hand side (pH 2) the degree of protonation corresponds to one, while on the right-hand side (pH 13) the degree of protonation is zero. For DAB-dendr-(NH₂)₆₄ the most important protonation microstates are also shown (top); a closed circle indicates a protonated site and an open circle a deprotonated state. The two-step protonation curve results from the stability of the intermediate onion-like protonation state, where 2/3 of the sites are protonated. Solid lines are best fits with the Ising model with parameters shown in Table 1.

Ising model

The protonation behavior of polyelectrolytes can be rationalized in terms of an Ising model [4-6, 8, 9]. Each of the N-ionizable sites can be characterized by a state variable sᵢ such that sᵢ = 0 corresponds to a deprotonated site and sᵢ = 1 to a protonated site. Including pair interactions only, the free energy of a given protonation state F relative to the completely deprotonated state can be written as

\[
\frac{F(s_1, \ldots, s_N)}{kT \ln 10} = \sum_i (pH - p\tilde{K}) s_i + \sum_{i < j} e_{ij} s_i s_j,
\]

where kT denotes thermal energy. In this equation we have introduced the following abbreviations: pH is the negative common logarithm of the proton activity (in M), p\tilde{K} the negative common logarithm of the microscopic dissociation constant of site i given all other groups are deprotonated, and e_{ij} > 0 characterizes the strength of the pair interactions between sites i and j. These pair interaction parameters are assumed to be nonzero for nearest neighbors only. A more extended explanation of the evaluation of the Ising model to the titration data of a branched polyelectrolyte is described in Ref. [6].

The simplest Ising model which describes the experimental titration data of the 1,4-diaminobutane poly(propylene imine) dendrimers in a satisfactory fashion involves four different microscopic pK values and three nearest-neighbor pair interaction parameters, see Fig. 2.

The microscopic pK values are denoted by p\tilde{K}⁰, p\tilde{K}³, p\tilde{K}⁵/², p\tilde{K}⁰, p\tilde{K}³ and p\tilde{K}⁵/². The outermost primary amines have the values p\tilde{K}⁰. We have three groups for the tertiary amines. The outermost shell of tertiary amine groups has p\tilde{K}³, the two innermost tertiary amines p\tilde{K}³, while all the remaining ones p\tilde{K}⁰.

The three pair interaction parameters are abbreviated as ε₁, ε₂ and ε₃. The outermost bonds between primary and tertiary amines have the value ε₁. The innermost bond, which consists of four carbons (1,4-diaminobutane), has the value ε₃. All remaining bonds have the value ε₂. The