



Sequestering ability of phytate towards protonated BPEI and other polyammonium cations in aqueous solution [☆]

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ABSTRACT

The interaction between protonated branched poly(ethylenimine) [BPEI] and phytate (1,2,3,4,5,6 hexakis (di-hydrogen phosphate) *myo*-inositol) [Phy] was studied potentiometrically. The measurements were carried out at $t=25\text{ }^{\circ}\text{C}$ and at low ionic strength values, without addition of supporting electrolyte, to avoid interferences with other anions and cations. In order to simplify the data treatment, BPEI was considered as a simple tetramine. Different species $\text{Phy}(\text{BPEI})_j\text{H}_j$, with $j=6,7,8$, and $\text{Phy}(\text{BPEI})_2\text{H}_7$ were found, having quite high stability. The ability of phytate to sequester BPEI was quantified by considering the parameter pL_{50} , namely the concentration ($-\log [\text{Phy}]_{\text{tot}}$) necessary to bind 50% of polyammonium cation (as trace). In our experimental conditions, for the system phytate–BPEI–proton we have $pL_{50}=7.01$, at $\text{pH}=7.4$ and $I=0.04\text{ mol L}^{-1}$. As for other phytate–polyammonium cation systems, the stability of the phytate–BPEI species is strictly proportional to the charges involved in the formation reactions. Therefore, it was possible to calculate the free energy contribution per bond, $\Delta G_{\text{b}}^{\text{U}}=4.4\pm 0.4\text{ kJ mol}^{-1}$. The dependence on temperature and ionic strength of the stability of phytate–low/high molecular weight polyammonium cations species, was studied using some semiempirical equations and enthalpy data for the protonation of both components. The dependence on temperature of the stability is quite low and the variation of pL_{50} in the range $15\leq t/^{\circ}\text{C}\leq 37$ is less than 0.5 log units. On the contrary, the effect of ionic strength is highly significant, with a lowering of pL_{50} of ≈ 2 log units ($I=0$ to 0.15 mol L^{-1}).

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1. Introduction

Natural organic matter (constituted to a great extent by macromolecules) is quite rich in functional groups which act as binding sites for inorganic and organic cations or anions over a wide pH range. The study of the physical and chemical properties of natural organic matter is very difficult owing to the fact that in these macromolecules, the protonation and complexation reactions depend on several factors, such as molecular weight, distance between functional groups, distribution of binding sites and structure (in terms of cross linking, etc.). To simplify the thermodynamic study of some natural organic molecules, such as humic and fulvic acids [1], often high molecular weight polyelectrolytes were chosen as model molecules in order to obtain information about the behaviour (acid–base properties and complexing ability) of natural macromolecules. The literature reports several thermodynamic data for the interaction properties of some high molecular weight polyelectrolytes [2–6]; in particular these data regard the acid–base properties of polycarboxylates and their

interactions with alkali, alkaline earth metals [2–5] and some low molecular weight polyamines [6]. Natural and biological fluids contain also amino compounds (amines, polyammonium cations, polyaminocarboxylates, etc.) that are among the fundamental molecules of biological interest, widely present in aminoacids, proteins and enzymes, and are responsible for the most of complex functions that make life possible. The biological function of natural polyelectrolytes is often mediated by interactions with other macromolecules such as, for example, proteins and natural surfactants (lipids). A very important example is the interaction of DNA with proteins. Among these macromolecules, polyammonium cations have a quite relevant role [7]. In the literature the interaction of polyammonium cations with carboxylic anions was widely reported, whilst a lesser number of data is reported for other ligands containing, for example, phosphate groups, despite their widespread involvement in biological systems. Few examples of phosphate complexation by synthetic polyammonium receptors in water were reported by Garcia-España et al. [8]; other papers also report [9–11] the enthalpy and entropy changes, which are important to interpret the main contribution for the stability of anion complexes in water.

The interaction of polyammonium cations with inorganic and organic polyanions [7–13] was mainly studied for low molecular weight molecules. In our previous papers, we already studied the

[☆] Speciation of phytate ion in aqueous solution. Previous parts of this series [18,28,40–44].

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interaction of different polyphosphates [13–16] and nucleotides [17] with biogenic amines. More recently the interaction of some poly-ammonium cations [ethylenediamine, 1,4-diaminobutane (putrescine), 1,5-diaminopentane (cadaverine), diethylenetriamine, *N,N'*-bis[3-aminopropyl]-1,4-diaminobutane (sperimine), *N*-[3-aminopropyl]-1,4-diaminobutane (spermidine), tetraethylenepentamine and pentaethylenhexamine] with phytate [18], some polymers, such as polyacrylate (MW=2 kDa), polystyrenesulphonates (MW=70 and 1000 kDa) and polyvinylsulphonate (MW=9 kDa) [2], and alginic and fulvic acids [19] were studied.

As a further contribution to the study of the acid–base properties and complexing ability of polyelectrolytes already undertaken [2–6], in the present paper we studied the interaction of an high molecular weight ammonium polyelectrolyte (branched polyethylenimine MW=750 kDa) with an high charged polyphosphate, such as phytate. This high molecular weight polyamine has a monomeric unit which contains primary, secondary and tertiary amino groups in the ratio 1:2:1, as shown in Fig. 1. It is a polymer obtained from the aziridine through ring-opening cationic polymerisation.

Poly(ethylenimine) [BPEI], has several applications in the biological, industrial and pharmaceutical fields [20–23]. For example, it is used in bioprocesses to facilitate the transfer of nucleic acids through biological membranes, for purification of DNA binding proteins, to transfer genes and oligonucleotides into living cells, as a flocculating agent and to immobilise enzymes and bacteria, as backbone of artificial enzymes. BPEI binds also heavy metal cations [24–26], and therefore can be used in several environmental applications [27].

Phytate [Phy], is widely present in nature and has an important biological activity; it modifies the bioavailability of several metal ions (such as calcium, iron, zinc, copper: see, e.g., [28] and references therein); it is regarded as the primary storage form of both phosphate and inositol in plant seeds and grains, and to be an antioxidant [28] and references therein]; it shows marked anticarcinogenic/antineoplastic properties; it may reduce and prevent kidney stone formation and it plays key roles in a number of crucial physiological activities, in addition to the treatment of different pathologies. Among its industrial and/or technological applications, very important is the use of phytate in remediation problems, such as the immobilisation and in-situ treatment of soils contaminated by many metals (including heavy metals and radionuclides).

Owing to their high charges, BPEI and phytate can be considered as model molecules for the study of the interactions between natural polycations and polyanions. The problems that can be encountered in such a study are connected to the interpretation/elaboration of the experimental data; different methods were used to explain the acid–base properties of BPEI: by applying the Ising model to short-range interactions [29], by relating the BPEI protonation with ion condensation [30] and by calculating the deprotonation quotient at different pHs [31]. In our previous work [23], we used a new approach to study the acid–base properties of BPEI; using this approach the branched poly(ethylenimine) was treated as a simple aliphatic tetramine. Since this

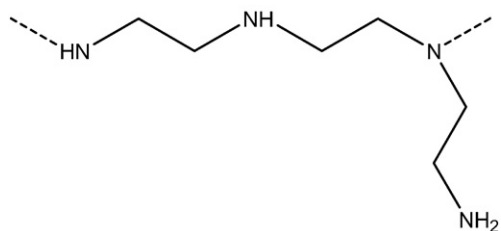


Fig. 1. Representation of BPEI monomeric unit.

Table 1
Protonation constants of BPEI at different ionic strength and temperatures

Species	log $K_i^{H^+a}$						
	$t=25\text{ }^\circ\text{C}$			$t=15\text{ }^\circ\text{C}$		$t=37\text{ }^\circ\text{C}$	
	$I=0^b$	$I=0.04^b$	$I=0.15^b$	$I=0^c$	$I=0.15^c$	$I=0^c$	$I=0.15^c$
BPEIH	9.36	9.39	9.49	9.65	9.78	9.04	9.17
BPEIH ₂	7.90	8.09	8.29	8.18	8.57	7.58	7.98
BPEIH ₃	5.29	5.62	5.85	5.50	6.05	5.06	5.63
BPEIH ₄	1.80	2.23	2.46	1.88	2.52	1.72	2.39

^a According to Eq. (4).

^b Ref. [23].

^c Calculated by empirical equations (refs. [34–37]).

approach is suitable to describe the acid–base properties of BPEI, it was used for studying its complexation with phytate.

2. Experimental section

2.1. Chemicals

All the reagents were Fluka analytical grade. A 50% aqueous solution of BPEI was used without further purification; its concentration was determined by potentiometric titrations, assuming the ligand as a monomer. Phytic acid solutions were prepared by weighing pure dipotassium salt $K_2H_{10}Phy$ (Fluka). Hydrochloric acid working solutions were prepared by diluting concentrates, and standardized against sodium carbonate. Tetraethylammonium hydroxide solutions were prepared from concentrated Et_4NOH (Fluka puriss. Electrochemical grade) and standardized against potassium biphthalate. All the solutions were prepared by using analytical grade water ($R \geq 18\text{ M}\Omega\text{ cm}^{-1}$) and preserved from atmospheric CO_2 by means of soda lime traps. Grade A glassware was employed.

2.2. Apparatus

The potentiometric measurements were carried out by using a potentiometer (Metrohm mod. E605) coupled with a combined ISE-H Orion Ross type glass electrode (mod. 8172), and with an automatic titrant dispenser (Metrohm Dosimat mod. 665). The potentiometer and the dispenser were connected to a PC and a suitable home made software allows monitoring of the titrations. The program allows the equilibrium potentials to be read and determination of the titrant volume to be added, based on the actual buffering properties of the solution under titration, so that the differences in successive readings were of ~ 0.1 as $-\log[H^+]$. The estimated precision of the system was $\pm 0.15\text{ mV}$ in the e.m.f. and $\pm 0.003\text{ ml}$ in the titrant volume. The measurement cell was thermostatted at $t=25 \pm 0.2\text{ }^\circ\text{C}$, and pure nitrogen presaturated with an ionic media solution at the same ionic strength of the working solution, was bubbled into the solution in order to avoid O_2 and CO_2 interference. The solutions were magnetically stirred.

Table 2
Protonation constants of phytate at different ionic strength and temperatures

Species	log $K_i^{H^+a}$						
	$t=25\text{ }^\circ\text{C}$			$t=15\text{ }^\circ\text{C}$		$t=37\text{ }^\circ\text{C}$	
	$I=0^b$	$I=0.04^b$	$I=0.15^b$	$I=0^c$	$I=0.15^c$	$I=0^c$	$I=0.15^c$
PhyH	18.17	17.24	9.41	18.25	9.50	18.08	9.31
PhyH ₂	15.32	14.73	9.67	15.38	9.73	15.25	9.60
PhyH ₃	12.76	12.41	9.33	12.78	9.35	12.73	9.30
PhyH ₄	10.05	9.96	7.97	10.06	7.98	10.03	7.95
PhyH ₅	7.59	7.54	6.35	7.59	6.35	7.58	6.34
PhyH ₆	6.13	6.12	5.10	6.12	5.10	6.13	5.10
PhyH ₇	3.52	3.52	2.75	3.49	2.56	3.55	2.62

^a According to the equilibrium: $H_iPhy^{(12-i)-} + H^+ = PhyH_{i+1}^{(12-i+1)-}$.

^b Ref. [40].

^c Calculated by empirical equations (refs. [34–37]).

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