Acid−Base Properties of Synthetic and Natural Polyelectrolytes: Experimental Results and Models for the Dependence on Different Aqueous Media[†]

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Protonation constants of several natural and synthetic humates and fulvates were determined by ISE-H^+ potentiometry in different ionic media (alkali metal halides and tetraethylammonium iodide) at different ionic strengths and $T = 298.15$ K. Experimental data obtained in previous studies of different synthetic (polyacrylates, polymethacrylates, polyacrylate-co-maleate) and naturally occurring (alginate, humic substances) polycarboxylates were also taken into account in the general analysis of acid−base properties of polyelectrolytes. Protonation constants were expressed as a function of the dissociation degree (α) using three models, namely, a simple linear model, the Högfeldt three-parameter equation, and the modified Henderson−Hasselbalch equation. Moreover, a model, independent of α, according to which acid−base properties of polyelectrolytes in the whole acidic pH range can be described by two protonation constants (Diprotic-like model), was also tested. This model allows us to analyze protonation and complex formation data as for simple low molecular weight ligands. In general, all the models taken into consideration give satisfactory results with fitting errors in the order Högfeldt three-parameter equation < Diprotic-like model < modified Henderson−Hasselbalch equation < simple linear model. For each type of polyelectrolyte investigated, a detailed discussion is reported. The parameters involved in the different models are strictly correlated, and canonical correlation analysis is reported. A statistical analysis on the protonation constants of all the polyelectrolytes investigated was made confirming that very similar results can be obtained using any considered model and, as a consequence, that the Diprotic-like model is a valid alternative simple approach to study acid−base properties of polyelectrolytes.

Introduction

The sequestering capacity of natural and synthetic polyelectrolytes toward heavy metal and organo-metal cations is well-known as shown by the abundance of papers reported in the literature and books published on this topic.[1−4] Synthetic polyelectrolytes, in particular polyacrylates and polymethacrylates, are used as flocculants in drinking water production, as scale inhibitors, as dispersants in papermaking, and as basic ingredients in the ion-exchange polymer systems for metal ion sequestration. On the other hand, natural polyelectrolytes, like humic and fulvic acids, play a fundamental role in the mobilization and transport of trace elements in the environment, contributing to the maintenance of the biogeochemical cycles of metal ions in natural waters, soils, and sediments. Moreover, due to the natural abundance and the very low environmental impact of these natural complexing agents, the interest of scientists is slowly moving to the possibility of using these natural low-cost biosorbents in the removing process of toxic heavy metals from industrial effluents.[5,6]

The study of metal−polyelectrolyte complexation cannot disregard the knowledge of the proton exchange capacity of the polyelectrolyte ligand, which is not easy to face in particular in the case of natural polyelectrolytes whose heterogeneous structure makes very complicated the modeling of protonation equilibria. The main difficulty when dealing with the protonation parameters of polyelectrolytes is their dependence on the conformation and, especially, on the charge of the molecules. In fact, the effective charge of the polyion is strictly dependent on the dissociation degree (α) of the macromolecule, and it results from the repulsive and attractive interactions between the charges of the different functional groups present in the macromolecular structure. Therefore, in this case, the acid−base equilibria cannot be studied, in principle, with the classical approach used for low molecular weight ligands. In the literature, there are many articles in which the authors propose different physicochemical approaches to explain the acid−base properties of polyelectrolytes of natural origin using different ways of calculation. As expected, most of the investigations concern the acid−base properties of humic and fulvic acids, which are by far the most important binding fractions of natural organic matter.[7−22] For these macromolecules, the heterogeneity of the structure, where different binding sites are present (mainly −COOH and −OH groups with a low content of −NH and −SH, this last when humic substances are formed under anoxic conditions), together with the electrostatic effects make calculations more complicated. The proposed literature models for humic and fulvic acids can be divided in two categories: (i) continuous models[7−11] in which a continuous distribution of

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protonation constants log *K* is considered and (ii) discrete models[12−19] according to which the macromolecule is supposed to contain a series of discrete sites with different log *K* values. Moreover, a further distinction can be done among the cited models, if electrostatic interactions are considered including one or more electrostatic terms.

Some examples of the first category of models are the nonideal competitive adsorption model (NICA)[9] and the NICA−Donnan model.[10,11] The most common models that belong to the latter category are the models V and VI [17,18] and the Stockolm Humic model (SHM).[19] Moreover, the Gibbs−Donnan model was also used to investigate the protonation dissociation of alginic acid,[20] and an electrostatic double layer model was applied in studying acid−base properties of some fulvic acids.[21,22] In general, it can be affirmed that each model used is valid for each system investigated, but nothing let us suppose that each model could be used successfully for any system under study. In other words, there is no evidence for a physicochemical model of general validity useful to describe the chemical behavior of any naturally occurring polyelectrolyte system. In this light, we present here some different approaches in the study of acid−base properties of different synthetic and natural polyelectrolytes with the aim to understand (i) if it is possible to obtain converging results on the systems investigated using the different models here considered and (ii) if it is possible to obtain satisfactory results, with a reduced difficulty in calculations, by using a more simple model as a valid alternative to the classical approaches. During the past few years, a systematic study on the acid−base behavior of natural and synthetic polyelectrolytes was carried out in our laboratories[23−31] using three different classical models according to which protonation parameters were considered as a function of the dissociation degree (α), namely: (i) simple linear model, (ii) modified Henderson−Hasselbalch equation,[32,33] and (iii) Högfeldt three-parameter equation.[34]

In this work, we report an extensive collection of new and already published protonation data[23,24,26−29] obtained by applying the above-mentioned models on different polyelectrolytes. In particular, we report data on the protonation of synthetic (polyacrylates, polymethacrylates, polyacrylate-co-maleate polymers, and humic acids synthesized in our laboratories) and natural (alginic acid extracted from *Macrocystis pyrifera brown algae*, humic and fulvic acids extracted from soils and sediments) polycarboxylates. Results obtained in the study of natural humic and fulvic acids were compared with those obtained from the investigation on the standard humic and fulvic acids supplied by the International Humic Substances Society (IHSS). For all the polyelectrolytes investigated, we tested a new model, namely, the "Diprotic-like model", in which the protonation parameters are independent of the dissociation degree of polyelectrolyte α.

According to this model, the polyelectrolyte is considered as a sum of difunctional monomeric units (in our case, dicarboxylic monomeric units), and its acid−base behavior is defined by two protonation constants, one for each functional group of monomer. Protonation constants of each polyelectrolyte under investigation, calculated using the four above-mentioned models, were determined in several ionic media (alkali metal chlorides and nitrates, tetraethyl ammonium iodide, artificial seawater) and at different ionic strengths or salinities. Investigations were carried out by potentiometry ([H$^+$]−glass electrode) at T = 298.15 K. In the case of humic and fulvic acids, in which phenolic groups are also present, we applied the above cited models in the acidic pH range (2.5 to 6.5), where, with a good approximation, the contribution of phenolic groups can be neglected. An experiment to consider also phenolic groups in the calculations was made in the pH range 3 to 10.5 and by considering the humic substances constituted of two monomeric units: the first one contains two carboxylic groups (analogously to the Diprotic-like model), and the second one contains a phenolic group. This last model was tested for some humate and fulvate samples. The dependence on ionic strength of protonation constants (according to the Diprotic-like model) was studied by using an extended Debye−Hückel-type equation, and thermodynamic protonation constants were calculated. Differences between protonation constants (according to the Diprotic-like model) obtained in alkali metal chlorides and those obtained in tetraethylammonium iodide were interpreted in terms of the formation of weak complexes between alkali metal ions and the polyelectrolyte. Some empirical equations are proposed with predictive purposes. All the models tested in this work gave good results when applied to the several polyelectrolytes here considered, and this is confirmed by the standard deviations on the fits of the four models. Moreover, the results of canonical correlation analysis applied on the parameters of different models confirm that they are strictly correlated.

Experimental Section

Chemicals. All reagents were of analytical grade. All solutions of natural and synthetic polyelectrolytes [polyacrylic (PAA) and polymethacrylic acids (PMA), poly(acrylic-co-maleic) acid (PAM), synthetic humic acids (HA S), humic acids (HA), fulvic acids (FA), alginic acid (AA)] were prepared from commercial products (Fluka or IHSS) or from products synthesized or extracted from natural samples in our laboratories. Ligand purity and water content, checked by potentiometric titrations and thermogravimetric analysis, respectively, were always taken into account. The two synthetic humic acids (HA-S1 and HA-S2) were synthesized in our laboratory according to the procedure reported by Pompe at al.[35,36] The reagents used in the synthesis 1 (xylose, glycine, and phenylalanine) and in the synthesis 2 (xylose and DL-glutamic acid monohydrate) supplied by Fluka (purissimum) were used without further purification.

Details on the characteristics, such as supplier companies, water content, and purity, of synthetic polyelectrolytes (PAA, PMA, and PAM) considered in this work are reported in refs 23 to 31. The elemental composition and the content of carboxylic and phenolic binding groups of natural polyelectrolytes here investigated (humic and fulvic acids) are reported in the corresponding section of the present work. Chloride and nitrate salts (Fluka, purity > 99.5 %), as well as the salt components of artificial seawater (alkaline and alkaline earth chlorides and sulfates by Fluka, purissimum, see next paragraph), were used as ionic media without further purification. Tetraethyl ammonium iodide was recrystallized twice from the methanol−acetone mixture, and the solvents were completely removed before use. Hydrochloric or nitric acid and sodium, potassium, lithium, or tetraethyl ammonium hydroxide solutions were prepared by diluting concentrated Fluka ampoules and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. All the solutions were prepared using freshly prepared and CO_2-free ultrapure water ($R \approx 18$ MΩ), and grade A glassware was always employed.

Apparatus and Procedure. The investigations on all polyelectrolytes were performed by potentiometric titrations ([H$^+$]−glass electrode) at (298.15 ± 0.1) K. The apparatus consisted of a model 713 Metrohm potentiometer, equipped with a

Table 1. Experimental Conditions for Potentiometric Titrations of the Synthetic Polyelectrolytes, at $T = 298.15$ K

polyelectrolyte	medium	I/mol·L^{-1}	C_L/mmol·L^{-1}[a]	runs	number of points	ref
HA-S1[b]	Et_4NI	0.1 to 0.75	0.2 to 0.3	8	142	this work
	LiCl	0.1 to 0.25	0.5 to 0.6	8	216	this work
	NaCl	0.1 to 0.4	0.2 to 0.5	9	179	this work
HA-S2[c]	Et_4NI	0.1 to 0.75	0.5 to 0.7	11	414	this work
	LiCl	0.1 to 0.4	0.2 to 0.3	9	301	this work
	NaCl	0.1 to 0.4	0.4 to 0.6	11	572	this work
PAA 2 kDa	$LiNO_3$	0.1 to 1.75				23
	$NaNO_3$	0.1 to 1.75				23
	Et_4NI	0.05 to 1				23
PAA 5.1 kDa	Et_4NI	0.1 to 0.75				24
	KCl	0.1 to 1.5				24
	LiCl	0.1 to 2				24
	NaCl	0.1 to 2				24
	SSWE	10 to 45[d]				26
PAA 20 kDa	Et_4NI	0.05 to 0.25				24
	KCl	0.1 to 0.5				24
	LiCl	0.1 to 1.5				24
	NaCl	0.05 to 1				24
	SSWE	10 to 45[d]				26
PMA 5.4 kDa	KCl	0.1 to 1.5				26
	LiCl	0.25 to 1.5				26
	NaCl	0.1 to 2				26
	SSWE	10 to 35[d]				26
PMA 4 kDa	Et_4NI	0.1 to 0.75				26
	KCl	0.1 to 2				26
	LiCl	0.1 to 1.5				26
	NaCl	0.1 to 2				26
	SSWE	25 to 45[d]				26
PAM 3 kDa	NaCl	0.05 to 1				27
	Et_4NI	0.1 to 0.5				27
PAM 70 kDa	NaCl	0.05 to 1				27
	Et_4NI	0.1 to 0.5				27

[a] Concentration of the polyelectrolytes. [b] Synthesized by xylose, glycine, and phenylalanine, according to the procedure by Pompe et al.[35,36] [c] Synthesized by xylose and DL-glutamic acid according to the procedure by Pompe et al.[35,36] [d] Salinity range.

combined glass electrode (Ross type 8102, from Orion) that had a resolution of ± 0.1mV and a reproducibility of ± 0.15 mV for cell voltage and a model 765 Metrohm motorized burette with a precision of ± 0.003 mL for titrant volume readings. The apparatus was connected to a PC, and automatic titrations were performed using a homemade computer program to control titrant delivery and data acquisition and to check for cell voltage stability. All titrations were carried out under magnetic stirring, and presaturated N_2 was bubbled through the purified solution to exclude O_2 and CO_2 inside. A volume of 25 mL of aqueous solution containing known amounts of protonated polyelectrolyte and the ionic medium in turn used to adjust the ionic strength at a pre-established value was titrated with a standard CO_2-free hydroxide solution. The following ionic media were used: Et_4NI, $NaNO_3$, $LiNO_3$, NaCl, KCl, and LiCl. The titrant was a hydroxide standard solution containing in turn the same cation of the ionic medium used. When the background salt was tetraethyl ammonium iodide, a tetramethy ammonium hydroxide standard solution was used as titrant. Moreover, a multicomponent ionic medium (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}) representative of the macro-composition of seawater[37,38] was used. This ionic medium (Synthetic Sea-Water for Equilibrium studies, SSWE) was already used by us, as a background salt, in speciation studies of several ligands, including polyelectrolytes.[25,26,29] The concentrations of components in mol·L^{-1} SSWE 35 salinity were: NaCl = 0.4221, Na_2SO_4 = 0.0288, KCl = 0.0110, $CaCl_2$ = 0.0111, and $MgCl_2$ = 0.0548. The composition for other salinity values was obtained by using the following equation: $m_s = m_{35}\ 27.56572\ S/(1000 - 1.005714\ S)$ in the molal concentration scale.[37] Polyelectrolyte solutions in SSWE ionic medium were titrated with sodium hydroxide. A different titrating procedure was adopted in exploiting the acid−base properties of alginic acid. In this case, owing to the low solubility of alginic acid in very acidic pH range, titrations were carried out starting from alkaline pH value (≈8.5), obtained by adding known amounts of hydroxide standard solutions, and the titrant was a standard solution of hydrochloric acid. For each experiment, independent titrations of a strong acid with standard hydroxide solutions were carried out under the same experimental conditions of the system investigated to determine the formal electrode potential $E°_{ext}$.

Details on the experimental conditions (ionic medium, ionic strength, polyelectrolyte concentration, runs, and number of titration points) for synthetic and natural polyelectrolytes investigated are given separately in Tables 1 and 13, respectively.

Calculations. BSTAC[39] and STACO[40] computer programs were used for the refinement of both protonation constants and all the parameters of an acid−base titration (E^0, log K_w, coefficient of junction potential j_a, analytical concentration of reagents). Computer program LIANA[41] was used to calculate the protonation constants of the polyelectrolytes under investigation with the different proposed models, to study the dependence on ionic medium and ionic strength of log K and to test some empirical predictive equations on the protonation and formation constants of polyelectrolytes. The PARVUS[42] computer program was used to perform canonical correlation analysis on the protonation parameters of the different polyelectrolytes, obtained with the proposed models.

Models Used for the Calculation of Protonation Constants of Polyelectrolytes. The study of protonation equilibria of polyelectrolytes

$$\mathrm{H}^+ + \mathrm{L}^z = \mathrm{HL}^{(z+1)} \tag{1}$$

and the determination of relative protonation constants

$$K = a_{\mathrm{HL}}/(a_{\mathrm{H}} \cdot a_{\mathrm{L}}) \tag{1a}$$

require the use of models that take into consideration the dependence of K on the dissociation degree of the polyelectrolyte, α

$$\alpha = [\mathrm{L}]/([\mathrm{HL}] + [\mathrm{L}]) = [\mathrm{L}]/[\mathrm{L}]_{\mathrm{T}}$$

In fact, by increasing α, the charge of polyelectrolyte increases, and consequently, the result is an increasing K value. The quantitative effect of charge of polyelectrolyte on protonation constant is given by

$$\log K = \mathrm{const} - \Delta G_{\mathrm{E}}/(RT \ln 10)$$

where ΔG_{E} is the Gibbs energy change for removing the proton against the electric field of polyelectrolyte surface.

The charge of polyelectrolytes z can be negative (L = anionic polycarboxylate, such as polyacrylate, polymethacrylate, etc.) or positive (L = polyammonium polyelectrolytes, such as polyallylamine). For carboxylic polyelectrolytes, the charge z is formally equal to −1, but the effective charge is generally < −1 (for example, for polyacrylate 2 kDa, $z = -2.14$), as already reported for polyacrylate.[29]

In both cases, the dependence of log K of polyelectrolytes on α and, consequently, on z can be taken into account by using two different equations: (i) the modified Henderson−Hasselbalch equation[32,33]

$$\log K = \log K_n - (n - 1)\log[(1 - \alpha)/\alpha] \tag{2}$$

and (ii) the three-parameter equation, based on the zeroth approximation,[43] proposed by Högfeldt[34]

Table 2. Protonation Constants of PAA 2 kDa Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.05	5.89	4.42	5.07	0.003	5.86	4.37	0.004	5.11	1.80	0.012	6.07	10.5	0.025
Et_4NI	0.1	5.74	4.34	4.98	0.003	5.72	4.30	0.004	5.01	1.76	0.011	5.92	10.17	0.025
Et_4NI	0.25	5.84	4.41	4.88	0.003	5.77	4.25	0.010	5.01	1.79	0.010	5.86	9.89	0.033
Et_4NI	0.75	5.44	4.45	4.93	0.002	5.43	4.44	0.002	4.94	1.53	0.009	5.73	10.05	0.019
Et_4NI	1	5.38	4.51	4.95	0.003	5.39	4.51	0.003	4.95	1.46	0.009	5.73	10.09	0.018
$LiNO_3$	0.1	5.37	4.32	5.13	0.004	5.46	4.50	0.019	4.98	1.51	0.011	5.85	10.27	0.014
$LiNO_3$	0.25	5.27	4.26	4.94	0.004	5.32	4.38	0.015	4.85	1.50	0.008	5.64	9.91	0.014
$LiNO_3$	0.5	5.05	4.25	4.71	0.002	5.07	4.28	0.009	4.68	1.41	0.003	5.38	9.49	0.016
$LiNO_3$	1	4.91	4.25	4.56	0.002	4.91	4.24	0.006	4.57	1.35	0.002	5.22	9.26	0.018
$LiNO_3$	1.25	4.86	4.25	4.52	0.001	4.85	4.23	0.005	4.54	1.33	0.002	5.17	9.19	0.018
$LiNO_3$	1.5	4.83	4.26	4.49	0.001	4.81	4.23	0.004	4.52	1.31	0.005	5.14	9.15	0.017
$LiNO_3$	1.75	4.58	4.15	4.54	0.002	4.63	4.28	0.007	4.46	1.18	0.011	5.06	9.08	0.011
$NaNO_3$	0.1	5.09	4.21	5.01	0.004	5.21	4.44	0.012	4.82	1.40	0.018	5.69	10.05	0.011
$NaNO_3$	0.25	5.01	4.11	4.91	0.006	5.13	4.32	0.013	4.72	1.43	0.020	5.56	9.79	0.011
$NaNO_3$	1.5	4.45	3.95	4.70	0.003	4.58	4.33	0.012	4.46	1.12	0.014	5.18	9.25	0.007
$NaNO_3$	1.75	4.47	4.01	4.65	0.002	4.57	4.33	0.009	4.45	1.12	0.011	5.17	9.24	0.009

[a] Std. dev. on the fit.

Table 3. Protonation Constants of PAA 5.1 kDa Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	6.27	4.33	5.17	0.004	6.22	4.26	0.006	5.24	2.03	0.017	5.89	10.23	0.019
Et_4NI	0.25	6.14	4.28	5.03	0.002	6.08	4.17	0.006	5.12	2.02	0.011	5.83	10.11	0.020
Et_4NI	0.5	6.02	4.32	5.01	0.002	5.97	4.22	0.006	5.09	1.93	0.009	5.72	9.97	0.016
Et_4NI	0.75	5.95	4.39	5.02	0.003	5.90	4.30	0.006	5.10	1.85	0.011	5.72	10.01	0.016
KCl	0.1	6.11	4.29	5.27	0.062	6.14	4.33	0.062	5.23	1.94	0.066	6.3	10.75	0.031
KCl	0.25	6.10	4.41	4.86	0.004	5.98	4.15	0.014	5.06	1.96	0.008	5.91	10.16	0.036
KCl	0.5	5.92	4.37	4.71	0.004	5.78	4.11	0.018	4.94	1.88	0.010	5.83	9.96	0.037
KCl	1	5.78	4.42	4.57	0.005	5.61	4.08	0.020	4.85	1.81	0.011	5.67	9.75	0.030
KCl	1.5	5.63	4.42	4.62	0.003	5.49	4.18	0.015	4.84	1.70	0.008	5.51	9.62	0.021
LiCl	0.1	6.03	4.45	5.33	0.018	6.06	4.51	0.018	5.28	1.80	0.024	6.06	10.59	0.020
LiCl	0.25	5.64	4.38	4.97	0.006	5.63	4.35	0.007	4.99	1.68	0.010	5.76	10.04	0.027
LiCl	0.5	5.44	4.36	4.72	0.011	5.39	4.24	0.013	4.81	1.60	0.013	5.49	9.63	0.021
LiCl	1	5.16	4.27	4.61	0.002	5.12	4.21	0.004	4.66	1.48	0.005	5.31	9.35	0.017
LiCl	1.5	5.02	4.32	4.54	0.007	4.98	4.24	0.008	4.61	1.39	0.007	5.18	9.2	0.015
LiCl	2	5.00	4.39	4.52	0.002	4.94	4.28	0.007	4.61	1.35	0.002	5.17	9.17	0.016
NaCl	0.1	6.29	4.54	5.13	0.004	6.20	4.36	0.013	5.28	1.97	0.010	6.1	10.56	0.024
NaCl	0.25	5.98	4.48	4.86	0.003	5.87	4.25	0.013	5.05	1.86	0.007	5.83	10.13	0.023
NaCl	0.5	5.77	4.45	4.71	0.001	5.64	4.20	0.014	4.92	1.77	0.007	5.66	9.84	0.025
NaCl	0.75	5.57	4.40	4.60	0.002	5.45	4.15	0.013	4.80	1.69	0.006	5.42	9.48	0.019
NaCl	1.25	5.41	4.31	4.56	0.001	5.31	4.12	0.010	4.72	1.63	0.005	5.35	9.37	0.016
NaCl	1.5	5.38	4.34	4.56	0.001	5.29	4.15	0.010	4.72	1.60	0.004	5.37	9.41	0.018
NaCl	1.75	5.36	4.34	4.57	0.001	5.27	4.17	0.010	4.72	1.59	0.005	5.37	9.4	0.018
NaCl	2	5.38	4.40	4.59	0.002	5.28	4.21	0.010	4.75	1.57	0.005	5.41	9.48	0.020
SSWE	10	5.02	4.28	4.91	0.007	5.11	4.45	0.012	4.78	1.34	0.015	5.39	9.67	0.015
SSWE	25	4.77	4.07	4.72	0.015	4.86	4.27	0.018	4.57	1.31	0.021	5.15	9.26	0.014
SSWE	35	4.70	3.99	4.64	0.022	4.79	4.19	0.024	4.49	1.32	0.026	5.07	9.12	0.013
SSWE	45	4.67	4.01	4.60	0.006	4.75	4.18	0.011	4.47	1.30	0.015	5.06	9.13	0.029

[a] Std. dev. on the fit.

$$\log K = \alpha^2 \log K_1 + (1-\alpha)^2 \log K_0 + 2\alpha(1-\alpha) \log K_m \tag{3}$$

In both eqs 2 and 3, log K is a not constant protonation parameter. In eq 2, n is an empirical parameter and K_n is the protonation constant at half-neutralization. In eq 3, K_1 and K_0 are the protonation constants at $\alpha \rightarrow 1$ and $\alpha \rightarrow 0$, respectively and K_m is an intermediate value which takes into account the nonlinearity of the function log K vs α.

The thermodynamic protonation constant, $\bar{K}$, is given by

$$\log \bar{K} = \int_0^1 \log K \mathrm{d}\alpha$$

For eq 2, we have $\log \bar{K} = \log K_n$, also indicated as the logarithm of the intrinsic protonation constant ($\log K_{\mathrm{int}}$) which defines the acid−base properties of polyelectrolytes.

For eq 3, we have $\log \bar{K} = (\log K_1 + \log K_0 + \log K_m)/3$.

When the function log K vs α is linear (Linear model)

$$\log K = \alpha \log K_1 + (1-\alpha) \log K_0 \tag{3a}$$

and, consequently, the thermodynamic protonation constant is

$$\log \bar{K} = (\log K_1 + \log K_0)/2 \tag{3b}$$

From $\alpha = 0.1$ to 0.9, the variation of protonation constants is not very large, for carboxylic polyelectrolytes, generally < 2.5 log units (this variation is < 1.5 log units in the α range 0.4 to 0.9). This suggests that a simple model which considers a dicarboxylic unit with two protonation constants (K_1 and β_2) should be independent of α, and it is sufficient to correctly explain the acid−base behavior of these macromolecules. In this case, the charge of polyelectrolytes z is formally equal to −2, but the effective charge is < −2; for example, for polyacrylate 2 kDa, we have $z = -3$ (see here later). Several tests on protonation data of different polyelectrolytes have shown that this Diprotic-like model is suitable, with a negligible loss of precision. A quite important result is that this model allows us to use all calculation methods for low molecular weight ligands also for polyelectrolytes.

In this case, the protonation constants are given by

$$K_i = [\mathrm{H}_i\mathrm{L}^{z+i}]/([\mathrm{H}_{i-1}\mathrm{L}^{z+i-1}][\mathrm{H}^+])$$

where L indicates the dicarboxylic unit, and consequently, the two protonation constants are expressed as

Table 4. Protonation Constants of PAA 20 kDa Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.05	7.86	4.60	5.71	0.003	7.69	4.28	0.019	5.98	2.81	0.015	6.73	11.35	0.008
Et_4NI	0.1	7.52	4.63	5.49	0.028	7.34	4.26	0.035	5.79	2.63	0.031	6.63	11.26	0.032
Et_4NI	0.25	7.21	4.49	5.33	0.003	7.06	4.14	0.017	5.60	2.53	0.014	6.45	10.98	0.031
KCl	0.1	6.55	4.60	5.23	0.001	6.44	4.38	0.011	5.41	2.10	0.007	6.35	10.89	0.031
KCl	0.25	6.19	4.45	4.94	0.009	6.07	4.20	0.015	5.14	1.98	0.011	5.93	10.25	0.024
KCl	0.5	6.00	4.55	4.69	0.044	5.81	4.19	0.048	5.00	1.86	0.045	5.76	9.98	0.025
LiCl	0.1	6.07	4.50	5.41	0.004	6.11	4.58	0.006	5.34	1.81	0.015	6.16	10.74	0.022
LiCl	0.25	5.71	4.41	5.07	0.002	5.72	4.42	0.002	5.07	1.69	0.010	5.84	10.21	0.020
LiCl	0.5	5.47	4.34	4.84	0.001	5.45	4.30	0.002	4.87	1.61	0.007	5.59	9.8	0.017
LiCl	1	5.24	4.37	4.64	0.002	5.19	4.27	0.006	4.73	1.49	0.004	5.39	9.46	0.021
LiCl	1.5	4.97	4.33	4.45	0.001	4.91	4.20	0.007	4.55	1.37	0.004	5.11	9.02	0.018
NaCl	0.05	6.59	4.64	5.56	0.020	6.58	4.60	0.020	5.59	2.04	0.025	6.47	11.19	0.030
NaCl	0.5	5.75	4.35	4.79	0.009	5.67	4.19	0.012	4.93	1.78	0.011	5.64	9.82	0.028
NaCl	1	5.66	4.46	4.63	0.010	5.53	4.19	0.017	4.86	1.71	0.012	5.57	9.73	0.029
SSWE	10	4.94	4.41	4.90	0.004	5.01	4.56	0.009	4.79	1.23	0.011	5.31	9.61	0.017
SSWE	25	4.63	4.17	4.69	0.001	4.72	4.36	0.009	4.54	1.19	0.012	4.99	9.14	0.027
SSWE	35	4.51	3.66	4.62	0.001	4.67	4.02	0.017	4.34	1.34	0.022	5.1	9.15	0.022
SSWE	45	4.44	3.05	4.48	0.001	4.64	3.58	0.020	4.11	1.54	0.028	4.98	8.99	0.013

[a] Std. dev. on the fit.

Table 5. Protonation Constants of PMA 5.4 kDa Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σa	log K_n	n	σ^a	log K_1	log β_2	σ^a
KCl	0.1	6.72	5.58	5.41	0.012	6.49	5.09	0.026	5.79	1.73	0.022	6.62	11.71	0.032
KCl	0.25	6.39	5.61	5.06	0.009	6.10	4.99	0.031	5.55	1.59	0.025	6.35	11.22	0.032
KCl	0.5	6.16	5.61	4.97	0.008	5.86	5.04	0.030	5.45	1.45	0.025	6.07	10.86	0.033
KCl	1	5.81	5.50	5.05	0.016	5.63	5.11	0.023	5.37	1.28	0.020	6.000	10.77	0.030
KCl	1.5	5.39	4.92	5.56	0.024	5.52	5.16	0.029	5.34	1.19	0.029	5.92	10.71	0.030
LiCl	0.25	5.71	5.40	5.13	0.009	5.59	5.12	0.017	5.35	1.24	0.020	5.99	10.85	0.025
LiCl	0.5	5.86	5.54	4.88	0.005	5.60	5.00	0.023	5.30	1.32	0.015	5.91	10.67	0.025
LiCl	1.5	5.27	5.13	5.19	0.013	5.27	5.13	0.013	5.20	1.08	0.013	5.67	10.38	0.025
NaCl	0.1	6.50	5.47	5.53	0.015	6.38	5.14	0.022	5.77	1.63	0.021	6.537	11.555	0.031
NaCl	0.25	6.19	5.51	5.18	0.010	5.99	5.06	0.025	5.53	1.49	0.021	6.268	11.14	0.026
NaCl	0.5	5.93	5.53	5.01	0.007	5.71	5.07	0.026	5.39	1.35	0.022	6.051	10.820	0.027
NaCl	1	5.66	5.47	5.05	0.012	5.50	5.14	0.020	5.32	1.19	0.017	5.86	10.66	0.026
NaCl	1.5	5.46	5.38	5.23	0.014	5.40	5.26	0.015	5.33	1.08	0.014	5.8	10.66	0.025
NaCl	2	5.39	5.28	5.44	0.017	5.42	5.35	0.018	5.38	1.03	0.018	5.82	10.76	0.026
SSWE	10	5.58	5.35	5.25	0.004	5.51	5.21	0.007	5.36	1.16	0.005	5.83	10.67	0.024
SSWE	25	5.30	5.28	5.10	0.006	5.25	5.16	0.009	5.20	1.05	0.008	5.57	10.4	0.014
SSWE	35	5.27	5.25	5.10	0.009	5.22	5.15	0.011	5.18	1.04	0.011	5.55	10.36	0.014

[a] Std. dev. on the fit.

$$K_1 = a_{HL}/(a_H \cdot a_L)$$

$$\beta_2 = a_{H_2L}/((a_H)^2 \cdot a_L)$$

By using the Diprotic-like model, the acid−base properties of a polyelectrolyte can be expressed by means of a mean protonation constant given by

$$\log \beta_{1/2} = (\log K_1 + \log K_2)/2$$

In the case of humic and fulvic acids, where phenolic groups are also present in the structure, this model can be used only in the acidic pH range (2.5 ≤ pH ≤ 6.5). In this pH range, with a good approximation, only the COOH groups are involved in acid−base equilibria. Moreover, if the calculations are extended to the basic part of titration curves (3 ≤ pH ≤ 10.5), it is necessary to suppose that the polyelectrolyte is formed by two different ligands (or monomeric units). The first unit contains two COOH groups, and the second contains a phenolic group. In this case, there are three protonation constants

$$K_1(L_1) = a_{H(L_1)}/(a_H \cdot a_{(L_1)})$$

$$\beta_2(L_1) = a_{H_2(L_1)}/((a_H)^2 \cdot a_{(L_1)})$$

Table 6. Protonation Constants of PMA 4 kDa Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	7.23	5.52	5.34	0.015	6.91	4.86	0.037	5.88	2.08	0.031	6.78	11.81	0.035
Et_4NI	0.25	7.17	5.53	5.22	0.014	6.82	4.80	0.040	5.81	2.05	0.032	6.7	11.66	0.035
Et_4NI	0.5	6.92	5.55	5.24	0.008	6.60	4.92	0.030	5.76	1.90	0.024	6.59	11.55	0.033
Et_4NI	0.75	6.69	5.55	5.32	0.009	6.44	5.05	0.028	5.74	1.74	0.021	6.53	11.52	0.031
KCl	0.1	6.62	5.54	5.37	0.011	6.40	5.07	0.025	5.74	1.69	0.021	6.52	11.53	0.031
KCl	0.25	6.35	5.53	5.05	0.008	6.06	4.99	0.029	5.52	1.58	0.023	6.31	11.14	0.031
KCl	0.5	6.00	5.42	5.08	0.011	5.80	5.02	0.024	5.41	1.42	0.019	6.09	10.83	0.028
KCl	1	5.72	5.23	5.14	0.018	5.62	5.02	0.020	5.32	1.32	0.017	5.97	10.66	0.029
KCl	1.5	5.45	4.91	5.47	0.020	5.55	5.09	0.021	5.32	1.24	0.021	5.93	10.64	0.029
KCl	2	5.41	4.76	5.63	0.024	5.57	5.12	0.031	5.34	1.23	0.032	5.94	10.67	0.031
LiCl	0.1	6.38	5.41	5.38	0.014	6.24	5.06	0.024	5.65	1.60	0.021	6.41	11.41	0.028
LiCl	0.25	6.09	5.41	5.06	0.008	5.89	4.95	0.023	5.42	1.50	0.018	6.11	10.91	0.027
LiCl	0.5	5.82	5.40	4.93	0.006	5.61	4.96	0.022	5.28	1.35	0.019	5.9	10.61	0.026
LiCl	1	5.45	5.14	5.01	0.013	5.36	4.96	0.016	5.16	1.21	0.013	5.71	10.34	0.025
LiCl	1.5	5.28	4.98	5.16	0.014	5.29	5.00	0.014	5.14	1.15	0.014	5.66	10.29	0.024
NaCl	0.1	6.52	5.47	5.43	0.013	6.34	5.12	0.025	5.73	1.64	0.022	6.47	11.50	0.028
NaCl	0.25	6.20	5.49	5.10	0.008	5.96	5.01	0.025	5.48	1.51	0.021	6.18	11.03	0.027
NaCl	0.5	5.92	5.45	5.02	0.007	5.72	5.02	0.025	5.37	1.38	0.020	5.99	10.78	0.025
NaCl	1	5.60	5.25	5.09	0.015	5.50	5.03	0.019	5.27	1.25	0.015	5.83	10.55	0.025
NaCl	1.5	5.39	5.07	5.33	0.017	5.42	5.12	0.017	5.27	1.16	0.017	5.8	10.56	0.025
NaCl	2	5.28	5.04	5.56	0.015	5.41	5.29	0.019	5.35	1.07	0.019	5.52	10.58	0.020
SSWE	25	5.49	5.10	5.25	0.035	5.48	5.07	0.035	5.27	1.22	0.035	5.76	10.44	0.033
SSWE	35	5.19	4.95	5.12	0.017	5.21	4.98	0.018	5.10	1.12	0.018	5.55	10.22	0.019
SSWE	45	4.89	4.40	5.30	0.006	5.09	4.81	0.024	4.95	1.14	0.026	5.44	10.11	0.018

[a] Std. dev. on the fit.

Table 7. Protonation Constants of PAM 3 kDa Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	7.199	3.899	4.398	0.026	6.81	3.18	0.063	4.99	2.94	0.064	6.13	10.08	0.034
Et_4NI	0.25	7.15	3.885	4.291	0.028	6.75	3.13	0.063	4.941	2.95	0.065	5.98	9.85	0.031
Et_4NI	0.5	6.922	3.856	4.335	0.028	6.58	3.2	0.063	4.886	2.8	0.058	5.89	9.70	0.028
NaCl	0.05	6.538	3.822	4.886	0.016	6.49	3.63	0.036	5.061	2.52	0.018	6.06	10.03	0.038
NaCl	0.1	6.343	3.786	4.67	0.016	6.2	3.56	0.036	4.873	2.41	0.022	5.89	9.77	0.017
NaCl	0.25	6.08	3.701	4.402	0.018	5.91	3.41	0.036	4.659	2.33	0.025	5.66	9.40	0.018
NaCl	0.5	6.008	3.693	4.23	0.020	5.81	3.32	0.036	4.56	2.32	0.028	5.50	9.11	0.017
NaCl	1	5.758	3.599	4.141	0.021	5.58	3.28	0.036	4.423	2.22	0.030	5.38	8.84	0.015

[a] Std. dev. on the fit.

Table 8. Protonation Constants of PAM 70 kDa Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	7.607	3.825	4.89	0.010	7.33	3.32	0.045	5.319	3.14	0.024	6.37	10.42	0.027
Et_4NI	0.25	7.455	3.814	4.718	0.012	7.15	3.25	0.045	5.195	3.07	0.024	6.25	10.24	0.027
Et_4NI	0.5	7.348	3.834	4.682	0.010	7.05	3.27	0.045	5.155	3.02	0.024	6.21	10.17	0.026
NaCl	0.05	6.59	3.941	5.229	0.032	6.57	3.93	0.036	5.247	2.4	0.023	6.23	10.30	0.040
NaCl	0.1	6.475	3.876	4.927	0.018	6.39	3.73	0.036	5.057	2.4	0.023	6.05	10.03	0.016
NaCl	0.5	6.322	3.836	4.291	0.020	6.07	3.35	0.036	4.704	2.44	0.023	5.81	9.66	0.019
NaCl	1	6.088	3.709	4.146	0.015	5.83	3.27	0.036	4.543	2.37	0.023	5.58	9.16	0.018

[a] Std. dev. on the fit.

$$K_1(L_2) = a_{H(L_2)}/(a_H \cdot a_{(L_2)})$$

Dependence on Ionic Strength of Protonation Constants. Experimental measurements were performed on all systems investigated at different ionic strengths in each ionic medium used. This allowed us to consider the dependence on ionic strength of protonation constants and to calculate the protonation constants at infinite dilution by extrapolation to 0 mol·L^{-1} ionic strength. The dependence on ionic strength of protonation constants of polyelectrolytes was taken into account using the following extended Debye–Hückel-type equation

$$\log \beta = \log {}^{T}\beta - z^{*}0.51 I^{1/2}(1 + 1.5 I^{1/2})^{-1} + CI \qquad (4)$$

where β is the overall protonation constant and ${}^{T}\beta$ is the relative value at infinite dilution. C is an empirical parameter for the dependence on I, and z^{*} can be expressed by

$$z^{*} = \sum (\text{charges})^{2}_{\text{reactants}} - \sum (\text{charges})^{2}_{\text{products}} \qquad (4a)$$

Since z^{*} (see eq 4a) is a function of z (effective charge), it can be refined by least-squares analysis of eq 4, together with the other parameters for the ionic strength dependence.

Results and Discussion

Synthetic Polyelectrolytes. The following synthetic polyelectrolytes were considered: PAA (2, 5.1, and 20) kDa; PMA (4 and 5.1) kDa; PAM (3 and 70) kDa. Moreover, two humic acids, HA S1 [elemental composition (%): C, 59.72; H, 5.13; O, 29.81; N, 5.34] and HA S2 [elemental composition (%): C, 56.71; H, 4.64; O, 34.05; N, 4.60] synthesized in our laboratories were also considered. For all the synthetic polyelectrolytes, the

Table 9. Protonation Constants of HA-S2[a] Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson–Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^b	log K_1	log K_0	σ^b	log K_n	n	σ^b	log K_1	log β_2	σ^b
Et_4NI	0.1	6.77	4.06	4.55	0.020	6.47	3.53	0.040	5.00	2.58	0.029	5.80	9.59	0.025
Et_4NI	0.5	6.26	3.75	4.27	0.023	6.01	3.31	0.035	4.66	2.45	0.025	5.88	9.73	0.026
Et_4NI	0.75	6.43	4.61	4.78	0.039	6.18	4.15	0.047	5.17	2.08	0.042	6.07	10.05	0.019
LiCl	0.1	6.47	4.01	4.57	0.064	6.24	3.61	0.068	4.92	2.41	0.065	5.62	9.45	0.018
LiCl	0.25	5.76	3.70	4.13	0.057	5.56	3.34	0.059	4.44	2.19	0.057	5.42	9.18	0.018
LiCl	0.4	5.47	3.87	3.97	0.050	5.35	3.22	0.052	4.32	2.02	0.051	5.33	9.08	0.015
NaCl	0.1	6.08	3.91	4.52	0.051	5.94	3.60	0.052	4.76	2.25	0.050	5.72	9.41	0.032
NaCl	0.25	5.89	3.74	4.05	0.018	5.63	3.28	0.031	4.45	2.26	0.021	5.64	9.19	0.026
NaCl	0.4	6.21	4.10	4.34	0.075	5.96	3.62	0.081	4.78	2.23	0.077	5.64	9.13	0.024

[a] Synthesized by xylose and DL-glutamic acid according to the procedure by Pompe et al.[35,36] [b] Std. dev. on the fit.

Table 10. Protonation Constants of HA-S1[a] Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson–Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^b	log K_1	log K_0	σ^b	log K_n	n	σ^b	log K_1	log β_2	σ^b
Et_4NI	0.1	6.95	5.2	5.05	0.077	6.63	4.57	0.086	5.6	2.07	0.079	6.15	10.92	0.027
Et_4NI	0.5	6.42	4.83	5.01	0.032	6.21	4.47	0.040	5.34	1.93	0.032	6.18	10.97	0.025
Et_4NI	0.75	6.7	5.71	5.66	0.033	6.53	5.36	0.038	5.95	1.61	0.035	6.34	11.24	0.028
LiCl	0.1	5.79	4.38	5.22	0.041	5.83	4.47	0.041	5.15	1.73	0.045	5.97	10.19	0.027
LiCl	0.25	6.44	4.05	4.81	0.040	6.32	3.74	0.041	5.04	2.33	0.044	5.94	9.85	0.024
NaCl	0.1	6.53	5.39	5.1	0.046	6.24	4.87	0.056	5.55	1.72	0.052	5.65	9.67	0.029
NaCl	0.25	5.98	4.14	4.57	0.015	5.81	3.85	0.023	4.82	2.05	0.013	5.58	9.24	0.039
NaCl	0.4	6.46	5.34	5.97	0.049	6.48	5.39	0.049	5.93	1.57	0.048	5.59	9.07	0.034

[a] Synthesized by xylose, glycine, and phenylalanine, according to the procedure by Pompe et al.[35,36] [b] Std. dev. on the fit.

Table 11. Protonation Constants (Calculated with the Diprotic-Like Model) of Synthetic Polyelectrolytes at $I \rightarrow 0$ mol·L^{-1}, Together with the Effective Charge and the Concentration of COOH Groups (as mmol·g^{-1}) of Macromolecules and the Parameter C of Equation 4, for the Dependence on Ionic Strength in Et_4NI and NaCl Ionic Media

polyelectrolyte	$-z$	COOH[a]	log K_1	C	log β_2	C
PAA 2 kDa	3.0	14	6.46 ± 0.06[b]	0.05 ± 0.03[b,c]	11.3 ± 0.1	0.16 ± 0.05[b,c]
				0.03 ± 0.01[d]	(4.84)[e]	0.10 ± 0.01[d]
PAA 5.1 kDa	4.5	14	7.09 ± 0.05	0.05 ± 0.03	12.34 ± 0.09	0.25 ± 0.04
				0.18 ± 0.01	(5.25)	0.40 ± 0.01
PAA 20 kDa	4.6	14	7.21 ± 0.04	−0.04 ± 0.05	12.56 ± 0.05	0.09 ± 0.08
				−0.8 ± 0.1	(5.35)	0.49 ± 0.08
PMA 4 kDa	3.7	11.6	7.28 ± 0.04	−0.03 ± 0.03	12.84 ± 0.07	0.14 ± 0.05
				0.02 ± 0.03	(5.56)	0.35 ± 0.02
PMA 5.4 kDa	4.4	11.6	7.44 ± 0.05	0.21 ± 0.02	13.28 ± 0.09	0.56 ± 0.04
				0.21 ± 0.01	(5.84)	0.55 ± 0.01
PAM 3 kDa	2.5	10.7	6.64 ± 0.01	0.22 ± 0.1	10.90 ± 0.02	0.36 ± 0.1
				−0.34 ± 0.10	(4.26)	−0.54 ± 0.11
PAM 70 kDa	2.5	10.7	6.87 ± 0.01	0.40 ± 0.1	11.22 ± 0.02	0.65 ± 0.1
				−0.30 ± 0.07	(4.35)	0.42 ± 0.03
HA-S1[f]	3.0	4.7	6.69 ± 0.08	1.04 ± 0.2	11.8 ± 0.10	1.73 ± 0.2
				−0.39 ± 0.02	(5.11)	−3.4 ± 0.5
HA-S2[g]	3.0	2.2	6.32 ± 0.01	1.18 ± 0.1	10.46 ± 0.02	1.96 ± 0.1
				0.6 ± 0.1	(4.14)	0.8 ± 0.1

[a] mmol·g^{-1}. [b] std. dev. [c] Parameter C of eq 4 in Et_4NI ionic media. [d] Parameter C of eq 4 in NaCl ionic medium. [e] Stepwise formation constant (log K_2). [f] Synthesized by xylose, glycine, and phenylalanine, according to the procedure by Pompe et al.[35,36] [g] Synthesized by xylose and DL-glutamic acid according to the procedure by Pompe et al.[35,36]

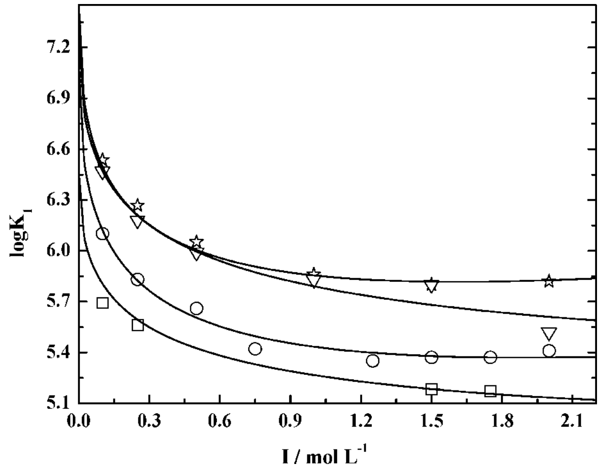

Figure 1. Dependence on ionic strength of log K_1 (according to the Diprotic-like model) of some synthetic polyelectrolytes (□, PAA 2 kDa; ○, PAA 5.1 kDa; ☆, PMA 5.4 kDa; ▽, PMA 4 kDa) in NaCl ionic medium and at $T = 298.15$ K.

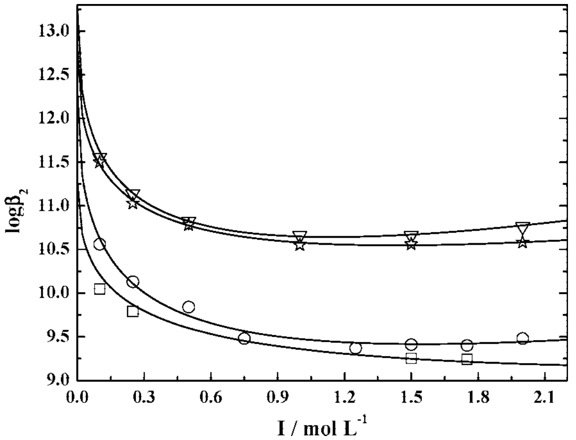

Figure 2. Dependence on ionic strength of log β_2 (according to the Diprotic-like model) of some synthetic polyelectrolytes (□, PAA 2 kDa; ○, PAA 5.1 kDa; ▽, PMA 5.4 kDa; ☆, PMA 4 kDa) in NaCl ionic medium and at $T = 298.15$ K.

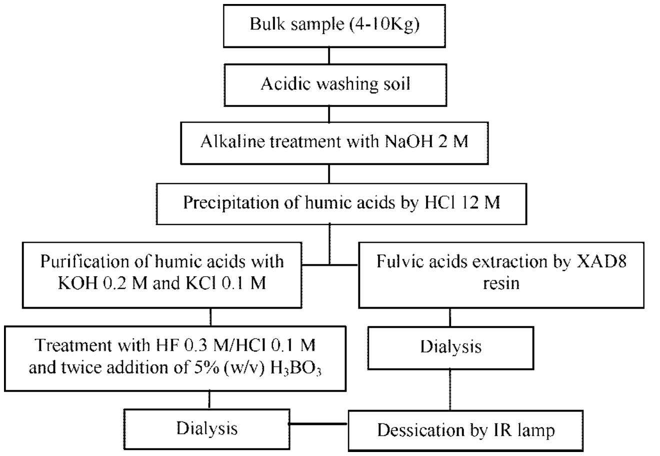

Figure 3. Procedure for extraction of humic and fulvic fractions from soil samples.

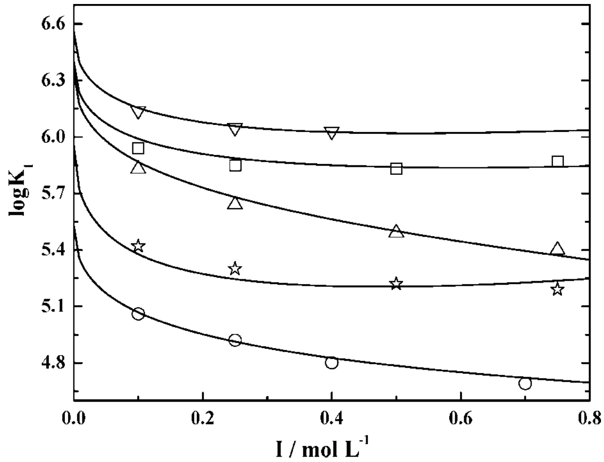

Figure 4. Dependence on ionic strength of log K_1 (according to the Diprotic-like model) of some natural polyelectrolytes (□, HA Ficuzza wood; ○, HA Nordic Lake; △, HA S. Cataldo; ▽, HA Piano Zucchi; ☆, FA Ficuzza wood) in NaCl ionic medium and at $T = 298.15$ K.

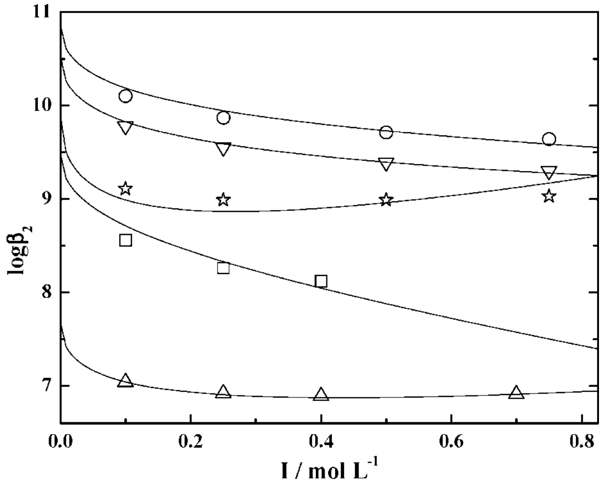

Figure 5. Dependence on ionic strength of log β_2 (according to the Diprotic-like model) of some natural polyelectrolytes (□, HA Pahokee peat; ○, HA Ficuzza wood; △, HA Nordic lake; ▽, HA S. Cataldo; ☆, FA Ficuzza wood) in NaCl ionic medium and at $T = 298.15$ K.

experimental conditions used in this work, together with those used in some previous investigations, are reported in Table 1.

By computer programs LIANA, BSTAC, and STACO, we calculated the protonation constants of polyelectrolytes in the ionic media and at the ionic strengths or salinities investigated. In Tables 2 to 10 are reported the values of protonation constants calculated using the four models considered here together with the standard deviation on the fit.

A first inspection on the protonation data for synthetic polyelectrolytes reported in Tables 2 to 10 shows a very good accordance between the log K_n values obtained by the modified Henderson−Hasselbalch equation and the average values (log $\beta_{1/2}$) by the Diprotic-like model. A quantitative correlation between log K values obtained by these two models and by the Högfeldt three-parameter equation and the linear model will be given for all the polyelectrolytes investigated, after the protonation of the natural polyelectrolytes will be discussed.

By using the extended Debye−Hückel equation (eq 4), we calculated the values of protonation constants of all the synthetic polyelectrolytes at infinite dilution ($I \rightarrow 0$ mol·L^{-1}), according to the Diprotic-like model. The results are reported in Table 11 together with the empirical parameter C of eq 4 in NaCl and in Et_4NI ionic media, the effective charge of polyelectrolytes, and the concentration (mmol·g^{-1}) of carboxylic groups.

As can be seen, there is a regular slight increase in log K_1 and log K_2 values, for each type of polyelectrolyte, with increasing molecular weight; e.g., log K_1 and log K_2 of PAA (2, 5.1, and 20) kDa are 6.46, 7.09, 7.21 and 4.84, 5.25, 5.35, respectively. The same consideration can be done for PMA and

Table 12. Elemental Analysis and mmol·g^{-1} of COOH and OH Groups in Humic and Fulvic Acids

samples	C[a]	H[a]	O[a]	N[a]	S[a]	P[a]	COOH[b]	OH[b]
			humic acids					
Fluka lot. 41968/1	56.06	4.05	32.60	0.93	1.35	-	4.00	6.6
Pahokee Peat lot.1S103H[c]	56.37	3.82	37.34	3.69	0.71	0.03	3.98	3.92
Nordic Lake lot.1R105H[c]	53.33	3.97	43.09	1.16	0.58	0.01	3.84	2.46
Ficuzza wood[d]	57.00	7.00	29.00	6.70	0.50	-	3.01	3.19
Piano Zucchi[d]	52.00	4.30	39.30	4.40	0.00	-	3.90	1.6
Cefalù[d]	52.43	3.38	35.69	3.30	0.20	-	4.50	4.8
S. Cataldo[d]	57.00	6.60	32.00	4.40	0.00	-	2.19	-
			fulvic acids					
Elliot soil II lot.2S102F[c]	50.12	4.28	42.61	3.75	0.89	0.12	4.18	1.14
Suwannee river II lot.2S101F[c]	52.34	4.36	42.98	0.67	0.46	0.004	5.41	1.45
Ficuzza wood[d]	47.00	5.90	42.00	4.50	0.90	-	2.45	-

[a] Elemental composition in %(w/w) of dry, ash-free samples. [b] Carboxylic and phenolic content in mmol·g^{-1}. [c] Data by IHSS. [d] Extracted from Sicilian soils.

Table 13. Experimental Conditions of Potentiometric Titrations, at T = 298.15 K

		I or S range	C_L			
polyelectrolyte	ionic medium	mol·L^{-1} or S	mmol·L^{-1}[a]	runs	no. of points	ref
AA	Et_4NI	0.1 to 1				28
	KCl	0.1 to 1				28
	NaCl	0.1 to 1				28
	LiCl	0.1 to 1				28
HA Fluka	NaCl	0.1 to 0.4	0.2 to 0.4	20	560	this work
lot. 41968/1	Et_4NI	0.1 to 0.75	0.2 to 0.5	14	374	this work
HA Pahokee Peat	Et_4NI	0.1 to 0.75	0.4 to 0.5	13	321	this work
lot. 1S103H[c]	NaCl	0.1 to 0.4	0.4 to 0.5	8	266	this work
HA Ficuzza wood[c]	Et_4NI	0.1 to 0.75	0.3 to 0.4	10	191	this work
	NaCl	0.1 to 0.75	0.3 to 0.4	13	248	this work
HA Nordic Lake	NaCl	0.1 to 0.7	0.4 to 0.5	11	276	this work
lot. 1R105H[c]	Et_4NI	0.1 to 0.75	0.4 to 0.5	11	272	this work
HA “S.Cataldo”[c]	NaCl	0.1 to 0.75	0.2 to 0.3	8	177	this work
	Et_4NI	0.1 to 0.75	0.2 to 0.3	7	137	this work
HA “Piano	NaCl	0.1 to 0.4	0.2 to 0.4	10	162	this work
Zucchi”	Et_4NI	0.1 to 0.75	0.3 to 0.4	14	180	this work
HA “Cefalù”[c]	Et_4NI	0.1 to 0.75	0.3 to 0.4	10	151	this work
	NaCl	0.1 to 0.25	0.3 to 0.4	4	63	this work
	LiCl	0.1 to 0.4	0.3 to 0.4	8	95	this work
FA “Ficuzza	NaCl	0.1 to 0.75	0.2 to 0.4	10	273	this work
wood”	Et_4NI	0.1 to 0.75	0.2 to 0.4	11	304	this work
FA Elliot soil	Et_4NI	0.1 to 0.75				29
II lot. 2S102F[b]	NaCl	0.1 to 0.75				29
	SSWE	5 to 45				29
FA Suwannee	NaCl	0.1 to 0.75	0.6 to 0.7	16	1062	this work
River II	$NaNO_3$	0.1 to 0.75	0.6 to 0.7	16	965	this work
lot. 2S101F[b]	Et_4NI	0.1 to 0.75	0.6 to 0.7	15	851	this work

[a] Concentration of the polyelectrolytes. [b] IHSS samples. [c] Samples extracted from Sicilian soils.

PAM polyelectrolytes (see Table 11). This trend was already noted in previous studies,[24] carried out by using the three-parameter model by Högfeldt et al.,[34] focused on the dependence of protonation constants on polyelectrolyte molecular weight.

Figures 1 and 2 show the dependence on ionic strength (NaCl medium) of log K_1 and log β_2 for some synthetic polyelectrolytes obtained using the Diprotic-like model according to eq 4.

The dependence on ionic strength of both log K_1 and log β_2 for all synthetic polyelectrolytes is almost the same, confirming the same acid−base behavior of this class of compounds in the same ionic medium.

Natural Polyelectrolytes. The acid−base properties of the following polyelectrolytes of natural origin were investigated: commercial alginic acid AA extracted from *Macrocystis pyrifera brown algae* (Aldrich), commercial humic acid (HA Fluka, lot. 41968/1), humic and fulvic acids (HA and FA) extracted from soils of different sites of Sicily [near Palermo (Ficuzza wood, Piano Zucchi), near Cefalù and near Caltanissetta (S. Cataldo)], following the classical extraction procedure proposed by Stevenson[2] and also recommended by the International Humic Substances Society. To reduce the reaction times, some steps of the procedure have been slightly modified by using more concentrated reagents. A scheme of this procedure is reported in Figure 3. All reagents used in the purification (NaOH, KOH, HCl, HF, H_3BO_3) were Fluka products of analytical grade.

To compare the acid−base properties of humic and fulvic acids extracted from Sicilian soil samples with reference samples, we also investigated the behavior of standard and reference soil and aquatic fulvic acids [Elliot soil II, lot. 2S102F, Suwannee river II, lot. 2S101F] and humic acids [Pahokee Peat, lot. 1S103H; Nordic Lake, lot. 1R105H], supplied by IHSS.

The elemental composition of humic and fulvic acids under investigation is reported in Table 12. In the same table is also reported the content of carboxylic and phenolic groups (as mmol·g^{-1}). The content of COOH and OH phenolic groups in the extracted samples was checked in our laboratories by direct potentiometric titrations. Afterward, to confirm the concentration values of the main two functional groups of humic substances, the classical calcium acetate method and barium hydroxide method[1−4,13] were used for all humic and fulvic samples. The

Table 14. Protonation Constants of Alginic Acid from *Macrocystis pyrifera brown algae* (AA) Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	5.19	2.5	3.12	0.143	4.62	2.15	0.155	3.38	2.31	0.151	4.51	6.85	0.006
Et_4NI	0.25	4.88	2.48	3.27	0.132	4.35	2.28	0.137	3.31	2.09	0.135	4.40	6.65	0.007
Et_4NI	0.50	5.27	2.78	3.59	0.060	4.28	3.04	0.093	3.66	1.64	0.098	4.42	6.70	0.011
Et_4NI	1.00	4.7	3.12	3.53	0.114	4.19	3.11	0.125	3.65	1.57	0.127	4.65	7.06	0.010
KCl	0.1	4.57	2.39	3.49	0.106	3.86	2.7	0.122	3.27	1.64	0.122	4.24	6.50	0.012
KCl	0.25	3.81	2.95	2.62	0.029	3.71	2.47	0.030	3.09	1.68	0.028	4.00	6.12	0.007
KCl	0.5	3.87	2.45	3.02	0.051	3.57	2.34	0.054	2.96	1.65	0.053	3.86	5.90	0.006
KCl	1.00	3.9	2.05	3.3	0.064	3.48	2.15	0.074	2.82	1.71	0.070	3.85	5.83	0008
NaCl	0.1	3.83	2.8	2.93	0.056	3.63	2.58	0.059	3.10	1.57	0.057	3.499	6.421	0.007
NaCl	0.25	3.88	2.14	3.55	0.063	3.44	2.49	0.084	2.96	1.51	0.077	3.247	6.008	0.008
NaCl	0.5	3.76	1.77	4.01	0.062	3.23	2.48	0.098	2.85	1.42	0.089	3.135	5.896	0.011
NaCl	0.75	3.71	1.45	4.59	0.063	3.16	2.3	0.087	2.73	1.44	0.081	3.060	5.743	0.008
LiCl	0.1	3.93	3.01	2.26	0.037	3.92	2.19	0.037	3.06	1.88	0.034	4.02	6.23	0.006
LiCl	0.25	4.17	1.8	3.97	0.066	3.64	2.21	0.085	2.93	1.73	0.078	3.74	5.81	0.008
LiCl	0.5	3.81	1.72	4.18	0.022	3.32	2.31	0.066	2.82	1.52	0.055	3.58	5.56	0.009
LiCl	1.00	3.42	1.69	4.41	0040	2.92	2.62	0.072	2.77	1.18	0.068	3.57	5.45	0.011

[a] Std. dev. on the fit.

Table 15. Protonation Constants of Humic Acid (HA) Fluka Lot. 41968/1 Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	6.35	4.57	5.10	0.006	6.25	4.33	0.019	5.28	1.97	0.009	6.14	10.55	0.016
Et_4NI	0.25	6.28	4.60	5.10	0.006	6.19	4.38	0.018	5.28	1.92	0.008	6.07	10.45	0.017
Et_4NI	0.75	6.60	4.74	5.13	0.006	6.47	4.39	0.027	5.41	2.05	0.006	6.16	10.58	0.014
NaCl	0.1	6.11	4.45	5.14	0.005	6.07	4.36	0.008	5.21	1.86	0.016	6.10	10.49	0.020
NaCl	0.25	6.24	4.54	5.06	0.005	6.16	4.33	0.017	5.23	1.93	0.009	6.01	10.34	0.019
NaCl	0.4	6.20	4.61	5.21	0.005	6.15	4.49	0.011	5.31	1.84	0.013	5.99	10.29	0.012

[a] Std. dev. on the fit.

Table 16. Protonation Constants of Humic Acid (HA) Pahokee Peat Lot. 1S103H Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	5.67	1.86	4.96	0.054	6.05	2.63	0.062	4.34	2.83	0.072	5.58	8.95	0.026
Et_4NI	0.25	6.09	3.36	4.35	0.044	5.98	3.11	0.047	4.55	2.51	0.043	5.55	8.92	0.024
Et_4NI	0.5	6.02	3.42	4.31	0.029	5.89	3.14	0.032	4.52	2.44	0.031	5.63	9.04	0.032
Et_4NI	0.75	6.33	3.76	4.36	0.037	6.13	3.31	0.042	4.71	2.48	0.037	5.76	9.23	0.026
NaCl	0.1	5.91	2.27	4.41	0.036	6	2.5	0.037	4.25	2.72	0.065	5.32	8.56	0.026
NaCl	0.25	5.42	2	4.24	0.033	5.56	2.39	0.034	3.98	2.62	0.047	5.18	8.26	0.029
NaCl	0.4	5.32	2.39	4.13	0.016	5.4	2.59	0.017	4.00	2.43	0.031	5.15	8.12	0.027

[a] Std. dev. on the fit.

Table 17. Protonation Constants of Humic Acid (HA) Nordic Lake Lot. 1R105H Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	5.66	1.21	4.27	0.030	5.86	1.86	0.034	3.88	3.02	0.053	5.20	7.18	0.024
Et_4NI	0.25	5.84	1.67	4.11	0.041	5.94	1.93	0.042	3.94	3.09	0.050	5.24	7.24	0.026
Et_4NI	0.5	5.98	2.45	3.95	0.037	5.9	2.27	0.038	4.09	2.88	0.040	5.42	7.52	0.026
Et_4NI	0.75	6.18	2.86	4.32	0.022	6.11	2.73	0.023	4.42	2.8	0.027	5.66	7.88	0.011
NaCl	0.1	5.35	1.31	4.41	0.020	5.64	2.11	0.027	3.89	2.87	0.040	5.06	7.04	0.018
NaCl	0.25	5.22	1.58	3.98	0.012	5.36	2.04	0.015	3.73	2.69	0.029	4.92	6.92	0.026
NaCl	0.4	5.13	1.74	3.87	0.028	5.23	2.09	0.028	3.68	2.62	0.034	4.80	6.89	0.014
NaCl	0.75	4.57	−0.95	4.74	0.013	5.19	1.61	0.030	3.44	2.78	0.043	4.69	6.91	0.013

[a] Std. dev. on the fit.

results of the direct and indirect analysis are comparable and are in good accordance with those provided by Fluka or by the IHSS company (see IHSS Web site and ref 16), especially for commercial humic substances.

Details on the experimental conditions (ionic medium, ionic strength, polyelectrolyte concentration, runs, and number of titration points) of potentiometric titrations of natural polyelectrolytes are given in Table 13.

Protonation constants of all the natural polyelectrolytes were determined in different ionic media and at different ionic strengths using the four above-discussed models. Results are reported in Tables 14 to 24.

As for the synthetic polycarboxylic ligands, also for naturally occurring polycarboxylates, the average values of protonation constants according to the Diprotic-like model (log $\beta_{1/2}$) and to the Högfeldt three-parameter equation [(log K_1 + log K_0 + log

Table 18. Protonation Constants of Humic Acid (HA) Extracted from Soil near Palermo (Ficuzza Wood) Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	6.19	4.65	5.04	0.047	6.05	4.43	0.049	5.24	1.88	0.047	6.04	10.33	0.038
Et_4NI	0.25	6.33	4.46	4.92	0.021	6.17	4.15	0.024	5.16	2.08	0.021	6.02	10.29	0.023
Et_4NI	0.5	6.3	4.43	5.01	0.096	6.19	4.18	0.096	5.19	2.07	0.097	6.09	10.40	0.036
Et_4NI	0.75	6.35	4.17	5.25	0.040	6.35	4.15	0.040	5.25	2.14	0.045	6.22	10.58	0.023
NaCl	0.1	5.86	3.48	5.26	0.042	6.03	3.89	0.044	4.96	2.12	0.051	5.94	10.10	0.026
NaCl	0.25	5.92	3.74	5.22	0.059	6.04	3.99	0.060	5.02	2.07	0.064	5.85	9.87	0.029
NaCl	0.5	5.66	3.15	4.98	0.043	5.82	3.56	0.045	4.69	2.19	0.050	5.83	9.71	0.040
NaCl	0.75	6.04	4.76	4.85	0.022	5.88	4.38	0.027	5.13	1.79	0.024	5.87	9.64	0.026

[a] Std. dev. on the fit.

Table 19. Protonation Constants of Humic Acid (HA) Extracted from Soil Near Caltanissetta (S. Cataldo) Site Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	6.45	4.49	4.27	0.060	6.12	3.63	0.068	4.87	2.3	0.062	5.93	9.89	0.028
Et_4NI	0.5	6.25	4.27	4.28	0.113	5.89	3.72	0.115	4.8	2.17	0.117	5.81	9.70	0.033
Et_4NI	0.75	5.72	4.73	4.86	0.011	5.62	4.48	0.015	5.05	1.6	0.012	5.82	9.73	0.013
NaCl	0.1	6.37	4.39	4.37	0.025	6.07	3.7	0.038	4.89	2.26	0.028	5.83	9.78	0.024
NaCl	0.25	5.93	4.46	4.28	0.045	5.63	3.86	0.051	4.74	1.94	0.046	5.64	9.55	0.028
NaCl	0.5	5.48	4.51	4.5	0.028	5.33	4.18	0.030	4.75	1.61	0.028	5.49	9.39	0.020
NaCl	0.75	5.28	4.17	4.46	0.011	5.18	4.02	0.015	4.6	1.63	0.010	5.40	9.30	0.022

[a] Std. dev. on the fit.

Table 20. Protonation Constants of Humic Acid (HA) Extracted from Soil Near Palermo (P. Zucchi Site) Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	6.31	4.29	5.14	0.028	6.27	4.17	0.028	5.22	2.07	0.030	6.19	10.59	0.025
Et_4NI	0.25	6.2	4.16	5.56	0.035	6.32	4.4	0.037	5.36	2.02	0.042	6.14	10.51	0.026
Et_4NI	0.5	6.26	4.56	5.11	0.031	6.18	4.34	0.032	5.27	1.96	0.031	6.18	10.56	0.027
Et_4NI	0.75	6.45	4.29	5.2	0.038	6.4	4.18	0.038	5.29	2.16	0.039	6.26	10.69	0.026
NaCl	0.1	5.94	4.18	5.31	0.023	6.02	4.35	0.025	5.19	1.86	0.028	6.14	10.48	0.026
NaCl	0.25	5.93	3.73	5.41	0.027	6.15	4.08	0.035	5.11	2.1	0.043	6.05	10.29	0.024
NaCl	0.4	6.03	3.84	5.29	0.090	6.15	4.07	0.090	5.1	2.08	0.093	6.03	10.20	0.033

[a] Std. dev. on the fit.

Table 21. Protonation Constants of Humic Acid (HA) Extracted from Soil near "Cefalù" Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	6.06	4.36	5.02	0.028	6	4.23	0.029	5.12	1.92	0.029	5.95	10.32	0.018
Et_4NI	0.25	6.04	4.41	4.97	0.024	5.97	4.23	0.025	5.1	1.91	0.024	5.89	10.23	0.020
Et_4NI	0.5	5.77	4.52	5.06	0.029	5.75	4.46	0.029	5.11	1.68	0.030	5.73	9.77	0.013
Et_4NI	0.75	5.86	4.55	5.12	0.009	5.83	4.49	0.009	5.16	1.7	0.012	5.99	10.39	0.011
NaCl	0.1	5.86	3.99	5.39	0.027	5.99	4.32	0.029	5.16	1.86	0.034	5.87	10.15	0.014
NaCl	0.25	5.71	4.19	4.93	0.022	5.7	4.18	0.022	4.94	1.8	0.026	5.77	9.93	0.016
LiCl	0.1	5.8	4.39	5.15	0.056	5.81	4.41	0.056	5.11	1.74	0.058	5.83	10.14	0.019
LiCl	0.25	5.63	4.31	4.76	0.033	5.57	4.18	0.033	4.87	1.72	0.033	5.72	9.92	0.013
LiCl	0.4	5.67	4.15	5.14	0.010	5.74	4.31	0.011	5.02	1.75	0.021	5.68	9.81	0.009

[a] Std. dev. on the fit.

K_m)/3] are in good accordance with the log K_n values calculated with the Henderson−Hasselbalch model.

The dependence of protonation constants on ionic strength has been considered also for natural polyelectrolytes by using eq 4. The values of the protonation constants at infinite dilution ($I \rightarrow 0$ mol·L^{-1}) were calculated, according to the Diprotic-like model, and are reported in Table 25 together with the empirical parameter C of eq 4, in Et_4NI and in NaCl ionic media. In the same table, the effective charge of polyelectrolytes and the concentration of carboxylic groups (as mmol·g^{-1}) are reported too. The results reported in Table 25 show a very similar proton exchange capacity of all humic and fulvic acids investigated: in fact, the values of log K_1 range within 1 log unit. A slightly different behavior can be noted for alginic acid. As expected, in accordance with results previously obtained in investigating acid−base properties of alginic acid[28] by the Högfeldt model, this naturally occurring polyelectrolyte shows values of protonation constants lower than those obtained for both humic and fulvic acids. In Figures 4 and 5, we report the dependence on ionic strength of log K_1 and log β_2 (according to the Diprotic-like model) of some natural polyelectrolytes in NaCl. Results obtained show very similar acid−base properties for all humic acids investigated in the acidic pH range.

Table 22. Protonation Constants of Fulvic Acid (FA) Elliot Soil II Lot. 2S102F Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ a
Et_4NI	0.1	5.46	2.24	4.27	0.035	5.6	2.51	0.037	4.06	2.63	0.047	5.23	8.27	0.011
Et_4NI	0.25	5.45	2.57	4.07	0.055	5.47	2.61	0.056	4.04	2.55	0.057	5.18	8.19	0.014
Et_4NI	0.5	5.94	3.71	3.72	0.066	5.53	3.07	0.077	4.29	2.32	0.069	5.25	8.30	0.014
Et_4NI	0.75	6.25	4	3.83	0.044	5.78	3.25	0.058	4.51	2.36	0.050	5.38	8.51	0.013
NaCl	0.1	5.43	2.17	4.51	0.063	5.67	2.6	0.066	4.13	2.62	0.071	4.97	7.16	0.011
NaCl	0.25	5.01	2.69	3.85	0.022	5.01	2.69	0.022	3.86	2.21	0.026	4.92	6.75	0.014
NaCl	0.5	4.98	3.04	3.57	0.031	4.86	2.72	0.034	3.79	2.11	0.030	4.96	6.50	0.010
NaCl	0.75	4.88	2.85	3.59	0.021	4.8	2.68	0.023	3.73	2.11	0.019	5.03	6.40	0.013
SSWE	5	4.87	2.89	3.39	0.009	4.71	2.57	0.015	3.64	2.14	0.010	4.73	8.06	0.019
SSWE	15	4.67	3.89	2.85	0.019	4.24	2.92	0.025	3.58	1.71	0.029	3.95	6.96	0.011
SSWE	25	4.49	4.15	3	0.002	4.15	3.14	0.035	3.65	1.53	0.019	4.31	7.59	0.017
SSWE	35	4.64	3.99	3.05	0.009	4.27	3.1	0.033	3.69	1.62	0.025	4.43	7.76	0.019
SSWE	45	4.69	4.19	3.07	0.018	4.28	3.26	0.042	3.77	1.55	0.036	4.18	7.35	0.005

[a] Std. dev. on the fit.

Table 23. Protonation Constants of Fulvic Acid (FA) "Suwannee River II Lot. 2S101F" Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	5.42	0.75	4.81	0.076	6	1.83	0.088	3.91	3.21	0.096	5.27	8.11	0.024
Et_4NI	0.25	5.88	2.35	4.29	0.070	5.97	2.42	0.070	4.19	2.91	0.068	5.47	8.43	0.024
Et_4NI	0.5	7.18	3.5	3.71	0.144	6.51	2.67	0.158	4.59	3.08	0.149	5.97	9.24	0.029
Et_4NI	0.75	8.86	4.59	3.64	0.230	7.76	2.85	0.259	5.29	3.64	0.249	6.53	10.14	0.035
NaCl	0.1	5.22	1.77	3.78	0.079	5.29	1.99	0.079	3.64	2.74	0.085	4.86	7.72	0.025
NaCl	0.25	5.15	2.11	3.67	0.052	5.16	2.14	0.052	3.64	2.59	0.057	4.70	7.62	0.029
NaCl	0.5	4.55	1.16	3.87	0.031	4.82	1.89	0.038	3.36	2.52	0.052	4.70	7.70	0.027
NaCl	0.75	4.81	2.06	3.63	0.022	4.87	2.19	0.027	3.53	2.42	0.022	4.92	7.90	0.033
$NaNO_3$	0.1	5.44	1.63	4.28	0.046	5.71	2.07	0.050	3.88	2.96	0.056	5.05	8.00	0.026
$NaNO_3$	0.25	5.23	1.4	4.2	0.052	5.52	1.94	0.057	3.73	2.92	0.064	4.96	7.96	0.027
$NaNO_3$	0.5	5.27	2.13	3.84	0.047	5.32	2.21	0.047	3.76	2.68	0.048	4.98	8.06	0.026
$NaNO_3$	0.75	5.19	1.69	3.86	0.033	5.31	1.98	0.034	3.65	2.75	0.040	5.16	8.24	0.028

[a] Std. dev. on the fit.

Table 24. Protonation Constants of Fulvic Acid (FA) Extracted from Soil near Palermo (Ficuzza Wood) Obtained with Four Different Models, in Several Ionic Media, at Different Ionic Strengths and at T = 298.15 K, Together with Standard Deviation on the Fit

	I	Högfeldt model				Linear model			Henderson−Hasselbalch model			Diprotic-like model		
ionic medium	mol·L^{-1}	log K_1	log K_0	log K_m	σ^a	log K_1	log K_0	σ^a	log K_n	n	σ^a	log K_1	log β_2	σ^a
Et_4NI	0.1	6.54	4.1	4.59	0.100	6.35	3.58	0.101	4.97	2.42	0.100	5.56	9.25	0.033
Et_4NI	0.25	5.5	1.88	4.4	0.052	5.68	2.43	0.053	4.08	2.63	0.061	5.58	9.30	0.015
Et_4NI	0.5	6.09	4.72	4.64	0.028	5.89	4.21	0.038	5.04	1.87	0.030	5.78	9.62	0.023
Et_4NI	0.75	6.45	4.43	4.88	0.031	6.28	4.07	0.036	5.17	2.16	0.031	6.04	10.03	0.014
NaCl	0.1	5.86	4.38	4.43	0.028	5.65	3.92	0.033	4.79	1.92	0.029	5.42	9.11	0.008
NaCl	0.25	5.5	3.98	4.27	0.031	5.39	3.61	0.033	4.51	1.9	0.031	5.30	8.99	0.013
NaCl	0.5	5.32	3.07	4.41	0.039	5.37	3.23	0.040	4.31	2.1	0.045	5.22	8.99	0.011
NaCl	0.75	5.24	3.74	3.93	0.020	5.08	3.35	0.027	4.22	1.91	0.020	5.19	9.03	0.013

[a] Std. dev. on the fit.

Contribution of Phenolic Groups in Acid−Base Properties of Humic and Fulvic Acids. Humic and fulvic acids contain several functional groups among which the relevant abundance of carboxylic and phenolic groups make them the most important groups in terms of acid−base properties of these macromolecules. As pointed out before (see paragraph on the Models Used for the Calculation of Protonation Constants of Polyelectrolytes), protonation equilibria of phenolic groups of humic substances were not considered analyzing potentiometric data in the acidic pH range (2.5 to 6.5). On the contrary, the protonation of phenolic groups must be taken into account when experimental titration data are analyzed also in the neutral−alkaline pH range. Therefore, the whole polyelectrolyte molecule is considered as a ligand containing two different binding units: the carboxylic one which behaves as a diprotic binding unit, responsible for the proton exchange in the acidic pH range, and the phenolic unit which accounts for the binding capacity of the polyelectrolyte in the pH range over 7. We tested this model on experimental data of three samples: two standard fulvic acids supplied by IHSS and the humic acid supplied by Fluka. The concentration of phenolic groups in the samples was obtained by direct and indirect titration (see previous section), and the results confirm those provided by the IHSS company (see Table 12). The protonation constant values of phenolic groups of the three humic substances in several ionic media and at different ionic strengths are reported in Table 26.

Ritchie et al.[16] made a systematic study of the acid−base properties of several standard and reference humic and fulvic acids of IHSS including the two samples here investigated. Authors used a modified Henderson−Hasselbalch model and calculated two protonation constants (log K_1 and log K_2), the first one attributed to the carboxylic groups and the other to the phenolic binding sites.

Table 25. Protonation Constants (Calculated in the Acidic pH Range with the Diprotic-Like Model) of Natural Polyelectrolytes at $I \to 0$ mol·L^{-1} and $T = 298.15$ K, Together with the Effective Charge and the Concentration of COOH Groups of the Ligand and the Parameters C of Equation 4 for the Dependence on Ionic Strength in Et_4NI and NaCl Ionic Media

polyelectrolyte	$-z$	COOH[a]	log K_1	C	log β_2	C
AA	3.5	5.7	5.18 ± 0.01[b]	0.98 ± 0.02[b,c]	7.93 ± 0.01[b]	1.67 ± 0.02[b,c]
				−1.049 ± 0.16[d]	(2.75)[e]	0.12 ± 0.09[d]
HA Fluka	2.0	4	6.51 ± 0.01	0.53 ± 0.10	11.11 ± 0.02	0.79 ± 0.10
				1.8 ± 0.2	(4.6)	3.3 ± 0.3
HA Pahokee Peat	2.0	3.98	5.93 ± 0.01	0.79 ± 0.03	9.48 ± 0.01	1.18 ± 0.03
				−0.44 ± 0.2	(3.55)	−1.1 ± 0.2
HA “Ficuzza wood”	2.0	3.01	6.40 ± 0.01	0.76 ± 0.11	10.86 ± 0.03	1.14 ± 0.11
				0.28 ± 0.05	(4.46)	−0.16 ± 0.07
HA “S. Cataldo”	2.1	4.00	6.35 ± 0.01	0.36 ± 0.03	10.53 ± 0.01	0.54 ± 0.03
				−0.23 ± 0.05	(4.18)	−0.03 ± 0.04
HA “Piano Zucchi”	2.0	3.9	6.56 ± 0.01	0.60 ± 0.08	11.14 ± 0.02	0.89 ± 0.08
				0.32 ± 0.06	(4.58)	0.12 ± 0.05
HA “Cefalù”	2.0	4.5	6.32 ± 0.01	0.57 ± 0.06	10.88 ± 0.02	0.85 ± 0.06
				0.47 ± 0.01	(4.56)	0.94 ± 0.03
HA Nordic Lake	2.1	3.84	5.53 ± 0.01	1.22 ± 0.03	7.68 ± 0.08	1.87 ± 0.03
				−0.02 ± 0.04	(2.15)	0.63 ± 0.04
FA Elliot soil II	2.5	4.18	5.68 ± 0.01	0.85 ± 0.03	8.99 ± 0.01	1.36 ± 0.03
				0.32 ± 0.05	(3.31)	1.9 ± 0.2
FA “Ficuzza wood”	2.9	2.45	5.96 ± 0.02	1.37 ± 0.05	9.89 ± 0.05	2.20 ± 0.05
				0.52 ± 0.06	(3.93)	1.5 ± 0.1
FA Suwannee river II	2.6	5.41	5.57 ± 0.01	2.59 ± 0.03	8.59 ± 0.01	4.18 ± 0.03
				0.26 ± 0.1	(3.02)	1.19 ± 0.06

[a] mmol·g^{-1}. [b] Std. dev. [c] Parameter C of eq 4 in Et_4NI ionic medium. [d] Parameter C of eq 4 in NaCl ionic medium. [e] Stepwise formation constants (log K_2).

Table 26. Protonation Constants of Phenolic Groups for FA Suwannee River II Lot. 2S101F, FA Elliot Soil II Lot. 2S102F, and HA Fluka Lot. 41968/1 in Several Ionic Media, at Different Ionic Strengths and at $T = 298.15$ K

samples	I / mol·L^{-1}	log K	σ[a]	log K	σ[a]	log K	σ[a]
		Et_4NI		NaCl		$NaNO_3$	
FA Suwannee River II lot.2S101F	0.1	9.56	0.03	9.26	0.01	9.16	0.01
	0.25	8.97	0.01	8.90	0.02	8.95	0.02
	0.5	8.92	0.01	8.81	0.02	8.84	0.01
	0.75	8.71	0.02	8.73	0.02	8.74	0.02
FA Elliot soil II lot.2S102F	0.1	9.99	0.01	9.75	0.03	-	-
	0.25	9.56	0.02	9.46	0.03	-	-
	0.5	-	-	9.37	0.04	-	-
	0.75	-	-	9.23	0.03	-	-
HA Fluka lot. 41968/1	0.1	10.51	0.03	10.37	0.04	-	-
	0.25	10.34	0.03	10.08	0.03	-	-
	0.4	-	-	9.77	0.04	-	-
	0.75	9.98	0.03	-	-	-	-

[a] Std. dev. on the fit.

Table 27. Formation Constants for Sodium Complexes of Natural and Synthetic Polyelectrolytes at $I = 0$ mol·L^{-1} and at $T = 298.15$ K

polyelectrolyte	log $K_1^{\mathrm{Na}a}$	log $K_0^{\mathrm{Na}a}$
PAA 2 kDa	−0.26 ± 0.03	1.08 ± 0.03
PAA 5.1 kDa	0.95 ± 0.05	2.27 ± 0.02
PAA 20 kDa	1.50 ± 0.02	2.95 ± 0.02
PMA 4 kDa	1.74 ± 0.07	2.65 ± 0.04
PAM 70 kDa	0.54 ± 0.03	1.66 ± 0.02
PAM 3 kDa	0.52 ± 0.04	1.52 ± 0.03
AA	1.25 ± 0.03	2.28 ± 0.02
HA Fluka lot. 41968/1	−0.11 ± 0.1	0.52 ± 0.09
HA Pahokee Peat lot. 1S103H	0.76 ± 0.03	1.53 ± 0.02
HA “Ficuzza wood”	0.68 ± 0.08	1.20 ± 0.06
HA “S. Cataldo”	−	0.86 ± 0.01
HA “Piano Zucchi”	0.37 ± 0.09	0.85 ± 0.06
HA “Cefalù”	0.58 ± 0.1	1.04 ± 0.06
HA Nordic Lake lot.1R105H	−	0.92 ± 0.01
HA S1	2.01 ± 0.1	2.8 ± 0.1
HA S2	0.77 ± 0.09	1.22 ± 0.06
FA Elliot soil II lot.2S102F	2.06 ± 0.08	2.53 ± 0.07
FA Ficuzza wood	−0.36 ± 0.1	0.99 ± 0.05
FA Suwannee river II lot.2S101F	0.10 ± 0.01	1.35 ± 0.01

[a] Referred to the reaction: Na + H_iL = NaH_iL.

In the same paper,[16] the authors report for the phenolic groups in fulvic acid from Elliot soil II a mean protonation constant of 9.53 in NaCl ionic medium at $I = 0.1$ mol·L^{-1}, very close to that (9.75) here obtained for the same standard certified material in the same conditions of ionic strength and medium (see Table 26). This is a further confirmation that our model and the Henderson−Hasselbach equation give very similar results, also in the alkaline pH range.

Dependence of Protonation Constants on Charge of Polyelectrolyte and on Carboxylic and Phenolic Groups Content. The protonation constant values of natural and synthetic polyelectrolytes in the acidic pH range (2.5 to 6.5) and at $I \to 0$ mol·L^{-1} reported in Tables 11 and 25, respectively, can be expressed as a function of the effective charge of polyelectrolyte and of the content of COOH groups (as mmol·g^{-1}). In the case of humic and fulvic acids, log K values are also a function of OH phenolic group content (as mmol·g^{-1}). The dependence of protonation constants on the effective charge of the molecule is well-known, while the dependence on mmol·g^{-1} of carboxylic and phenolic groups can be justified by considering that they are an index of the density of these functional groups in the polyelectrolytes and, consequently, of the distance between them. In light of these considerations, we propose the following equation

$$\log K_j = a_0 + a_1|z|^2 + a_2C_{\mathrm{carb}}^2 + a_3C_{\mathrm{phen}} \qquad (5)$$

where log K_j is the protonation constant of a polyelectrolyte (in turn log K_1, log K_2, or log $\beta_{1/2}$ according to the Diprotic-like model); a_0, a_1, a_2, and a_3 are empirical parameters; $|z|$ is the absolute value of effective charge; and C_{carb} and C_{Phen} are the concentrations (as mmol·g^{-1}) of COOH and OH phenolic groups.

For log K_1, log K_2, and log $\beta_{1/2}$, we obtain

$$\log K_1 = 5.99 + 0.03|z|^2 + 0.003C_{\mathrm{carb}}^2 + 0.02C_{\mathrm{phen}}$$

$$\log K_2 = 3.58 + 0.06|z|^2 + 0.003C_{\mathrm{carb}}^2 + 0.1C_{\mathrm{phen}}$$

$$\log \beta_{1/2} = 4.78 + 0.015|z|^2 + 0.0055C_{\text{carb}}^2 + 0.089C_{\text{phen}}$$

The standard deviations for calculated protonation constants are: 0.11, 0.10, and 0.09 for $\log K_1$, $\log K_2$, and $\log \beta_{1/2}$, respectively.

Equation 5 shows a good predictive power. In fact, if the effective charge and the concentration of carboxylic and phenolic groups of a polyelectrolyte are known, it is possible to calculate the relative protonation constants, according to the Diprotic-like model. In particular, if we consider an effective charge value $|z| = 1$, the protonation constant of the monomer unit of polyelectrolytes can be obtained using the empirical parameters calculated for $\log K_2$; for instance, if we consider PAA, where phenolic groups are absent, we obtain from eq 5 a value of $\log K_2 = a_0 + a_1 + a_2 14^2 = 4.23$ very close to $\log K = 4.26$ of (monomer) acrylic acid.[23] Analogously, if we apply eq 5 to humic and fulvic acids, we can obtain the $\log K_2$ of the carboxylic group of the hypothetical monomer unit of the natural polyelectrolyte: for FA Suwannee river II and for HA Pahokee Peat, we calculate $\log K_2$ values of 3.87 and 4.08, respectively. These values are comparable with the protonation constant of the carboxylic group of 3-hydroxybenzoic acid ($\log K = 4.08$ at $I = 0$ mol·L^{-1} and $T = 298.15$ K),[44] whose structure can be considered as representative of a building block of natural fulvic and humic acids.

Dependence on the Medium of Protonation Constants and Formation of Weak Complexes. The values of protonation constants of both carboxylic and phenolic groups of the polyelectrolytes obtained in alkali metal chlorides are noticeably lower than those obtained in tetraethyl ammonium iodide. This evident dependence of protonation parameters on the background salt can be explained by considering that tetraethylammonium salts do not interact significantly with carboxylic and phenolic ligands, while these ligands form weak complexes with alkali metal ions. In light of this consideration, by knowing the protonation constants in alkali metal chlorides and in Et_4NI, it is possible to calculate the formation constants of weak complexes ML (with M = alkali metal ions). In the case of a low molecular weight ligand

$$K = K'(1 + K^{\text{M}}[\text{M}]) \tag{6}$$

with K' being the apparent protonation constant and K^{M} being the formation constant of the alkali metal complex species. For $C_{\text{M}} \gg C_{\text{L}}$ (with C_{L} and C_{M} analytical concentration of the ligand and metal ion, respectively), eq 6 can be written as

$$K = K'(1 + K^{\text{M}}C_{\text{M}}) \tag{7}$$

Equation 7 can be also extended to polyprotic acids by using the calculation method reported in ref 26.

In Table 27, we report the formation constants (at $I = 0$ mol·L^{-1}, NaCl or $NaNO_3$ medium) of weak complexes K_i^{Na} formed by the polyelectrolytes investigated with sodium ions (K_i^{Na} refers to the reaction $\text{Na} + \text{H}_i\text{L} = \text{NaH}_i\text{L}$). These formation constants were calculated using the protonation constants $\log K_1$ and $\log \beta_2$ obtained with the Diprotic-like model. As can be seen, all polyelectrolytes form the NaL species with a $\log K_0^{\text{Na}}$ values ranging from 0.52 to 2.95, and almost all form the NaHL species with $\log K_1^{\text{Na}}$ that ranges from −0.36 to 2.06.

The stability of weak alkaline metal complexes in aqueous solution, irrespective of the ligand, is mainly due to electrostatic interactions. In light of this consideration, in a previous work[45] we suppose the existence of a correlation between the $\log K$ of the weak complexes and the charge of the ligand involved. By considering the stability constants of different alkaline metal−carboxylate complexes, we found a very simple relationship between the $\log K$ and the charge z of the carboxylate

$$\log K = \frac{1}{2}|z| + \frac{A}{|z|}$$

with $|z|$ being the absolute value of the charge and A being an empirical parameter that, in the case of the Na^+ cation, is −0.30. The predictive power of this equation, tested until now only on low molecular weight carboxylates, is quite good also for synthetic and natural high molecular weight polycarboxylates. In fact, by putting in the previous equation the effective charges of the polyelectrolytes reported in Tables 11 and 25, we calculated the $\log K^{\text{Na}}$ values which are in good accordance with the experimental ones; e.g., for $|z| = 2$ we calculate a $\log K_0^{\text{Na}}$ value of 0.85, very close to the experimental formation constants of polyelectrolytes with $z \approx -2$, i.e., HA Fluka, HA S. Cataldo, HA Piano Zucchi, HA Nordic Lake (see Table 27). Slight discrepancies between calculated and experimental values are observed in some cases probably due to the uncertainty on the charge values calculated for some polyelectrolytes.

Table 28. Canonical Correlation Analysis between Different Models Used in This Work

independent variables		coefficients and dependent variables				
y_1	y_2	a_0	a_1x_1	a_2x_2	a_3x_3	explained variance %
			Synthetic Polyelectrolytes			
$\log K_1$		0.60	$0.45 \log K_1$	$0.44 \log K_0$	$0.09 \log K_m$	99.4
	$\log \beta_2$	0.28	$1.02 \log K_1$	$0.41 \log K_0$	$0.54 \log K_m$	99.4
$\log K_1$		0.29	$0.98 \log K_n$	$0.31n$		99.3
	$\log \beta_2$	0.39	$1.98 \log K_n$	$-0.15n$		99.3
$\log K_1$		0.59	$0.66 \log K_1$	$0.32 \log K_0$		99.3
	$\log \beta_2$	0.23	$0.91 \log K_1$	$1.06 \log K_0$		99.3
			Natural Polyelectrolytes			
$\log K_1$		1.05	$0.39 \log K_1$	$0.44 \log K_0$	$0.05 \log K_m$	90.2
	$\log \beta_2$	0.61	$1.11 \log K_1$	$0.27 \log K_0$	$0.55 \log K_m$	90.2
$\log K_1$		0.55	$0.89 \log K_n$	$0.41n$		89.9
	$\log \beta_2$	0.66	$1.94 \log K_n$	$0.23n$		89.9
$\log K_1$		0.97	$0.66 \log K_1$	$0.23 \log K_0$		89.9
	$\log \beta_2$	0.44	$0.85 \log K_1$	$1.09 \log K_0$		89.9
			All Polyelectrolytes			
$\log K_1$		0.71	$0.46 \log K_1$	$0.07 \log K_0$	$0.42 \log K_m$	98.0
	$\log \beta_2$	0.36	$1.10 \log K_1$	$0.33 \log K_0$	$0.52 \log K_m$	98.0
$\log K_1$		0.31	$0.96 \log K_n$	$0.37n$		97.9
	$\log \beta_2$	0.48	$1.98 \log K_n$	$-0.21n$		97.9
$\log K_1$		0.68	$0.68 \log K_1$	$0.28 \log K_0$		97.8
	$\log \beta_2$	0.27	$0.88 \log K_1$	$1.09 \log K_0$		97.8

Table 29. Statistical Data for Protonation Parameters of All Polyelectrolytes Obtained with Different Models at $I = 0.1\ \mathrm{mol \cdot L^{-1}}$ in Et_4NI and NaCl Ionic Media and at $I \rightarrow 0\ \mathrm{mol \cdot L^{-1}}$, at $T =$ 298,15 K

model	parameter	mean value
	Et_4NI 0.1 mol·L^{-1}	
Höegfeldt	log K_1	6.4 ± 0.7[a]
	log K_0	4 ± 1
	log K_m	4.8 ± 0.4
	(log K_1 + log K_0 + log K_m)/3	5.0 ± 0.7
Linear	log K_1	6.3 ± 0.5
	log K_0	2.4 ± 0.5
	(log K_0 + log K_1)/2	5.0 ± 0.6
Diprotic-like	log K_1	5.9 ± 0.4
	log β_2	9.6 ± 1.0
	log $\beta_{1/2}$	4.9 ± 0.6
Henderson−Hasselbalch	log K_n	5.0 ± 0.6
	n	3.6 ± 0.9
	NaCl 0.1 mol·L^{-1}	
Höegfeldt	log K_1	6.0 ± 0.4
	log K_0	4 ± 1
	log K_m	4.8 ± 0.5
	(log K_1 + log K_0 + log K_m)/3	4.9 ± 0.6
Linear	log K_1	6.0 ± 0.3
	log K_0	3.8 ± 0.9
	(log K_0 + log K_1)/2	4.9 ± 0.6
Diprotic-like	log K_1	5.7 ± 0.4
	log β_2	10 ± 1
	log $\beta_{1/2}$	4.8 ± 0.6
Henderson−Hasselbalch	log K_n	4.9 ± 0.6
	n	2.1 ± 0.4
	$I \rightarrow 0$ mol·L^{-1}	
Diprotic-like	log K_1	6.4 ± 0.6
	log β_2	11 ± 1.5

[a] ± Std. dev.

Canonical Correlation Analysis and Statistical Consideration. A number of dependent variables (n) can be expressed as a function of some independent variables (m, $m \geq n$), by canonical correlation analysis[42]

$$y = a_0 + a_1x_1 + a_2x_2 + ... + a_mx_m \tag{22}$$

We performed several calculations to check the correlation between different protonation parameters obtained by different models. Results of this analysis are reported in Table 28. For both synthetic and natural polyelectrolytes, a strong correlation can be noted between different protonation parameters, and we think that this correlation can also be used for predictive purposes. In other words, by using parameters for canonical correlation, it is possible to find protonation parameters for a model if the ones for a different model are known.

The great number of systems investigated allowed us to carry out also a statistical analysis of data obtained on protonation parameters. The mean values of the protonation constants calculated by using the different models for all polyelectrolytes investigated at $I = 0.1\ \mathrm{mol \cdot L^{-1}}$, in Et_4NI and NaCl media and at $I \rightarrow 0\ \mathrm{mol \cdot L^{-1}}$, are reported in Table 29 with the relative standard deviation.

Among the different protonation constants characterizing the acid−base properties of the various systems investigated, the K_1 is of greater interest in the investigation on the behavior of polyelectrolytes in natural aquatic systems where the pH value ranges from 6 to 8.5.

From the analysis of log K_1 values reported in Table 29, the following considerations can be made: (i) as the log K_1 values from the Högfeldt and Linear models are the same, the Högfeldt model can be certainly linearized in the $0.5 \leq \alpha \leq 1$ range; (ii) this allows us to affirm that it is possible to use a model according to which K_i are independent of α; (iii) the value of log K_1 obtained using the Diprotic-like model, where the dependence on α is not taken into account, is the same (within the error) as that obtained from the Högfeldt and Linear models, and therefore, it can be used as the others to reach the same result; (iv) the similarity of the mean values of log K_1 obtained with the different models at $I = 0.1\ \mathrm{mol \cdot L^{-1}}$ in Et_4NI and in NaCl can be extended also at other ionic media and ionic strengths; (v) a further comparison between the parameters reported in Table 29 can be done by considering the mean log K values (log $\bar{K}$) that correspond to (log K_1 + log K_0 + log K_m)/3 for the Högfeldt model, (log K_0 + log K_1)/2 for the Linear model, log $\beta_{1/2}$ for the Diprotic-like model, and log K_n in the case of the Henderson−Hasselbalch model. Similarly to the log K_1 values, also the log $\bar{K}$ values obtained with the different models are the same within the errors. To evidence the similarity between log $\bar{K}$ values obtained with different models, linear correlations between log $\beta_{1/2}$ and (log K_1 + log K_0 + log K_m)/3 and between log $\beta_{1/2}$ and log K_n in NaCl at different ionic strengths, for all the natural and synthetic polyelectrolytes, are reported in Figure 6a and b, respectively. In both cases, the correlation between the parameters is very good, as confirmed by the correlation coefficients R that are 0.94 and 0.95.

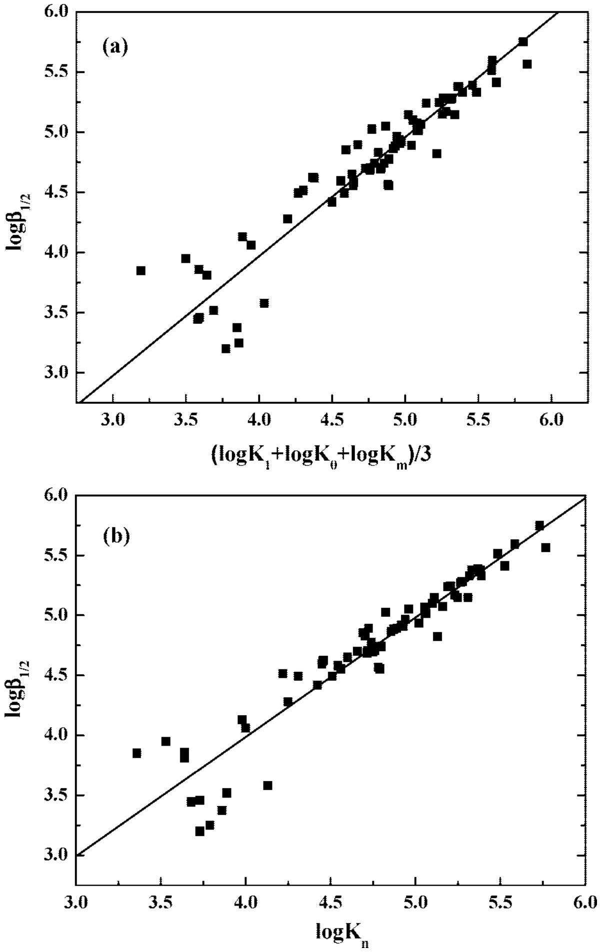

Figure 6. Linear correlation between log $\beta_{1/2}$ and (log K_1 + log K_0 + log K_m)/3 (a) and log $\beta_{1/2}$ and log K_n (b) for all the polyelectrolytes, in NaCl ionic medium, at different ionic strengths and $T = 298.15$ K.

Conclusions

The acid−base properties of several synthetic and naturally occurring organic polyelectrolytes containing both carboxylic and phenolic binding sites have been investigated using different chemical models.

The possibility of using a simple model according to which (i) the binding capacity of carboxylic groups can be described by two protonation constants (Diprotic-like model) independent of the dissociation degree of the polyelectrolyte and (ii) the phenolic groups behave as a second ligand in the alkaline pH range was also discussed.

The similarity of results obtained by all the models tested, within the experimental errors, lets us affirm that each of the models investigated can be used to define the acid−base properties of both synthetic and naturally occurring polyelectrolytes with comparable results if the standard deviation on the fit is considered, according to the trend: Högfeldt three-parameter equation < Diprotic-like model < modified Henderson−Hasselbalch equation < simple linear model.

As shown by canonical correlations and statistical analysis of data, the results obtained by the Diprotic-like model are in very good accordance with those obtained using other models based on the dependence of protonation constants on α (three-parameter model by Högfeldt and the classical Henderson−Hasselbach model). Therefore, the more simple Diprotic-like model can be used as a valid alternative model in investigating acid−base properties of polyelectrolytes.

The dependence of protonation constants on ionic strength has been evaluated using an extended Debye−Hückel equation by means of which the empirical parameters for the ionic strength dependence and the charge of the polyelectrolyte were calculated for all the systems investigated.

The dependence on ionic medium was also considered taking into account the weak interaction of polyelectrolytes with the sodium ion. To this end, a relationship, where the sodium formation constant is correlated to the charge of the low molecular weight carboxylic ligand, was used, as an extension, to predict, with a good approximation, the values of sodium−polyelectrolyte formation constants.

A predictive equation for the calculation of protonation constants of polyelectrolytes has been proposed based on the effective charge of the polyion and on the content of carboxylic and phenolic groups.

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