Polyacrylate Protonation in Various Aqueous Ionic Media at Different Temperatures and Ionic Strengths

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The protonation constants of the polyacrylate anion (molecular mass 2000 Da) in Et_4NI, Me_4NCl, LiCl, $LiNO_3$, NaCl, $NaNO_3$, and KCl aqueous solution, were determined in a wide range of ionic strengths. A three-parameter approximation was used to express protonation constants as a function of the dissociation degree α, and their dependence on ionic strength was considered using a simple polynomial expansion. Differences in log K^H between different data in different media were interpreted in terms of weak complex formation between polyacrylate and alkali metal cations. Measurements were also performed at different temperatures ($15 \le T/°C \le 55$) in order to calculate enthalpy and entropy changes for the protonation of the polyacrylate. Thermodynamic parameters for the protonation of monomer, acrylic acid, were studied potentiometrically at different temperatures and ionic strengths for purposes of comparison.

Introduction

Investigations into the acid−base properties of polycarboxylic ligands are of great importance in studying the speciation of natural waters, where −COOH groups arising from biochemical processes of degradation of the organic matter and from different fractions of humic substance (Thurmann and Malcom, 1983) are always present. In particular the soluble fulvic fraction of humic acids contains several carboxylic groups often distributed among the alkyl chain and aromatic rings (Buffle, 1988; Anderson et al., 1990). As reported by Gamble and Schnitzer (1973), most fulvic fractions found in soils are polyelectrolytes with molecular weight and chemical property ranges comparable to those of synthetic polyelectrolytes, such as poly(acrylic acid) (PAA). Therefore, a study of the acid−base behavior of polyacrylate ligands can indirectly give useful information about the ligand capacity of humic substances. Pioneering studies on the physicochemical properties of polyelectrolytes, such as electrostatic surface potential and molecular symmetry, were performed by Katchalsky (1950, 1954), Katchalsky et al. (1954), Fuoss (1954), and Marcus (1955). Marinsky (1966, 1973, 1976, 1983) and Marinsky et al. (1982, 1983) studied the dependence on electrostatic potential of the apparent protonation constant of polyacrylate anion by using ion exchanger resins; these authors also reported results on protonation and complexation equilibria with metal ions in separated phase. The interaction between polyacrylate anion and calcium ion was also studied by Iida (1996) in order to evaluate the influence of polymeric membranes on the activity of calcium ion in KCl aqueous solution.

From the point of view of acid−base properties, the study of polyelectrolytes may be considered as an extension of the studies of simple electrolytes, the most important distinction being the high charge of the polyion and, therefore, the high values assumed by the electrostatic potential of the whole molecule, which makes studying ion charge interaction more complicated. In some cases, especially when dealing with high molecular weight polycarboxylates, such as PAA with 20 000 Da or more, the effects produced by the interaction of ionic charges do not vanish even at infinite dilution, as they do in solutions of simple electrolytes. Therefore, in defining acid−base properties of polyelectrolytes, it becomes very important to establish effective charge availability in different pH ranges of the titration curves.

A simple model reducing the complexity of the polyelectrolyte system was proposed by Högfeldt et al. (1989) to compare experimental and calculated log *K* values of linear polycarboxylates, such as carboxymethyldextran [$I = 0.1$ mol L^{-1} (NaCl) at $T = 25$ °C] and poly(acrylic acid), [$I = 0.005$ to 0.1 mol L^{-1} (NaCl) at $t = 15$ °C]. The so-called "three-parameter model" describes the whole system by means of three log K^H values as a function of dissociation degree (α), as reported in

$$\log K^H = \log K_1{}^H\,\alpha^2 + \log K_0{}^H(1-\alpha)^2 + 2\log K_m{}^H\,\alpha(1-\alpha) \quad (1)$$

where $\log K^H = pH + \log[(1-\alpha)/\alpha]$, log $K_1{}^H$ is the protonation constant of polyacrylate anion when $\alpha \rightarrow 1$; log $K_0{}^H$ is the protonation constant of polyacrylate anion when $\alpha \rightarrow 0$; log $K_m{}^H$ is an intermediate value (which accounts for the nonlinear behavior of the function log K^H vs α). We can determine the integral free energy of proton dissociation expressed as an equilibrium constant log $\bar{K}^H$, by using the simple equation

$$\log \bar{K}^H = \int_0^1 \log K^H(\alpha)\,d\alpha = (1/3)(\log K_1{}^H + \log K_0{}^H + \log K_m{}^H) \quad (2)$$

On the basis of the above considerations, in this paper we report a potentiometric study ($[H^+]$-glass electrode) on the protonation of polyacrylate anion having average molecular weight of 2000 Da, i.e., containing ∼27 carboxylic groups. Protonation constants were determined by using

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Table 1. Experimental Details of Potentiometric Measurements

ligand	ionic medium	C_L/mmol L^{-1}	I/mol L^{-1}	T/°C
polyacrylic acid	Et_4NI	10−20	0.05−0.75	25
	Me_4NCl	9−18	0.05−1.75	25
	NaCl	5−25	0.05−3.0	25
	LiCl, KCl,	5−25	0.05−2.0	25
	$NaNO_3$, $LiNO_3$	10−20	0.1−1.5	
acrylic acid	Et_4NI	10−20	0.1−1	15−55
polyacrylic acid	NaCl	9−18	0.05−1.0	15−55

the above-reported “three-parameter model” (eqs 1 and 2). To evaluate the salt effect on the protonation of polyacrylate ligand, the investigations were carried out in the aqueous ionic media Et_4NI and Me_4NCl, by assuming that tetraalkylammonium salts do not interact (or interact very weakly) with carboxylic ligands, according to the literature data (Daniele et al., 1985; De Robertis et al., 1993), and in LiCl, $LiNO_3$, NaCl, $NaNO_3$, and KCl, in a wide range of ionic strength.

Thermodynamic parameters, $\Delta H°$ and $T\Delta S°$, were obtained from protonation data at different temperatures, $15 \leq T/°C \leq 55$. Moreover, for purposes of comparison, the acid−base properties of the monomer, acrylic acid, were studied potentiometrically, at different temperatures and ionic strengths.

Experimental Section

Materials. All reagents were of analytical grade. All solutions of poly(acrylic acid)s were prepared from commercial products by Fluka and Aldrich. Ligand purity, checked by potentiometric titrations and thermogravimetric analysis (water content), was always taken into account. Tetraalkylammonium salts were recrystallized from methanol−acetone, and solvent was completely eliminated before use. Sodium, lithium, and potassium chlorides and nitrates (Fluka, purissimum) were used without further purification. Hydrochloric acid and sodium or tetramethylammonium hydroxide titrant solutions were standardized against sodium carbonate and potassium biphthalate, respectively. Tetramethylammonium hydroxide solutions were used when background salt was a tetraethyl- or tetramethylammonium salt. All the solutions were prepared using analytical grade water (R = 18 MΩ cm^{-1}) and grade A glassware was employed.

Experimental Equipment and Procedure. The measurements were carried out using potentiometric apparatus consisting of a Metrohm Model 665 automatic titrant dispenser coupled with a Metrohm Model 654 potentiometer and a combination Orion-Ross 8172 glass electrode. The estimated accuracy of this system was ±0.15 mV and ±0.003 cm^3 for emf and titrant volume reading, respectively. In titration cells pure nitrogen was bubbled through the solutions in order to avoid O_2 and CO_2 inside, and the solutions were magnetically stirred. A volume of 20−25 mL of solution, containing poly(acrylic acid) and the background salt in order to adjust the ionic strength to different values, was titrated with hydroxide solutions (NaOH, Me_4NOH). Some experimental details of potentiometric measurements are reported in Table 1. For each experiment, independent titrations of acidic solutions (HCl or HNO_3) with NaOH or Me_4NOH solutions were performed, in the same experimental conditions of ionic strength and temperature as the systems under study, for determining the formal electrode potential (readings in terms of pH = −log [H^+]). All titrations were carried out up to pH ~7. Owing to the toxicity of poly(acrylic acid) (the main organ targets are eyes and blood), some precautions, such as protective glasses and mask, have been taken in handling this compound when preparing the solutions.

Table 2. Protonation Constants of Polyacrylate Anion (PAA) as a Function of Ionic Strength (I/mol·L^{-1}) and Dissociation Degree (α), in Different Ionic Media Salts, at T = 25 °C

		log K^{H} [a]						
α	I/mol L^{-1}	Et_4NI	Me_4NCl	$NaNO_3$	NaCl	KCl	$LiNO_3$	LiCl
0.1	0.05	4.71	4.62	4.67	4.67	4.65	4.67	4.70
0.1	0.10	4.67	4.57	4.61	4.61	4.60	4.62	4.65
0.1	0.25	4.63	4.49	4.53	4.53	4.51	4.53	4.56
0.1	0.50	4.65	4.46	4.46	4.46	4.43	4.43	4.47
0.1	0.75	4.72	4.48	4.43	4.43	4.39	4.39	4.41
0.1	1.00	4.82	4.50	4.42	4.42	4.37	4.36	4.37
0.1	1.25		4.54	4.41	4.42	4.36	4.34	4.38
0.1	1.50		4.58	4.42	4.42	4.36	4.34	4.39
0.1	1.75		4.62		4.43	4.38		4.43
0.1	2.00				4.44	4.40		4.49
0.1	2.50				4.49			
0.1	3.00				4.55			
0.5	0.05	5.40	5.27	5.28	5.28	5.28	5.29	5.28
0.5	0.10	5.33	5.17	5.16	5.16	5.16	5.17	5.16
0.5	0.25	5.23	5.03	4.98	4.98	4.98	4.96	4.96
0.5	0.50	5.18	4.95	4.84	4.83	4.83	4.76	4.77
0.5	0.75	5.20	4.93	4.77	4.76	4.76	4.66	4.68
0.5	1.00	5.26	4.95	4.73	4.72	4.72	4.60	4.61
0.5	1.25		4.97	4.71	4.70	4.71	4.55	4.58
0.5	1.50		5.00	4.70	4.70	4.71	4.54	4.58
0.5	1.75		5.02		4.70	4.72		4.60
0.5	2.00				4.71	4.74		4.63
0.5	2.50				4.74			
0.5	3.00				4.78			
0.9	0.05	6.49	6.25	6.11	6.13	6.14	6.05	6.10
0.9	0.10	6.42	6.13	5.92	5.96	5.97	5.84	5.91
0.9	0.25	6.28	5.93	5.64	5.68	5.69	5.50	5.57
0.9	0.50	6.16	5.81	5.42	5.45	5.47	5.21	5.26
0.9	0.75	6.14	5.76	5.31	5.33	5.36	5.05	5.09
0.9	1.00	6.18	5.75	5.25	5.27	5.30	4.95	4.99
0.9	1.25		5.76	5.21	5.22	5.27	4.88	4.94
0.9	1.50		5.78	5.18	5.21	5.24	4.84	4.93
0.9	1.75		5.80		5.19	5.24		4.95
0.9	2.00				5.19	5.24		4.99
0.9	2.50				5.19			
0.9	3.00				5.19			

[a] 3(±std dev) = 0.01−0.03.

Calculations. The nonlinear least squares computer program ESAB2M (De Stefano et al., 1987) was used in order to determine all the parameters of an acid−base titration (analytical concentration of the reagents, electrode potential, junction potential coefficient j_a, ionic product of water K_w). The computer program LIANA (De Stefano et al., 1997) was used for the calculation of protonation constants, together with parameters for dependence on ionic strength and on temperature.

Results and Discussion

Protonation Constants. By assuming that the acid−base behavior of a polyelectrolyte can be considered as an extension of a simple electrolyte, the association equilibrium of a polyelectrolyte can be simply expressed by

$$A^- + H^+ = HA$$

and its apparent protonation constant can be expressed as a function of dissociation degree

$$\log K^H = pH + \log[(1 - \alpha)/\alpha]$$

where

$$\alpha = [A^-]/([A^-] + [HA])$$

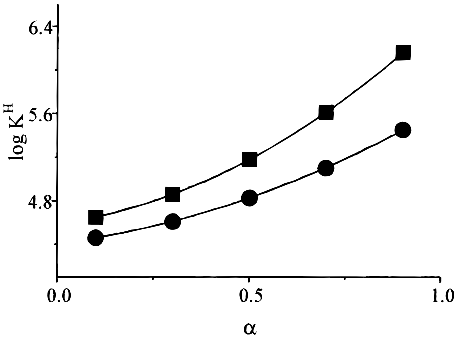

Figure 1. Protonation constants of polyacrylate anion (PAA) as a function of dissociation degree (α) in Et_4NI (■) and NaCl (●) ($I = 0.5$ mol L^{-1}, $T = 25$ °C).

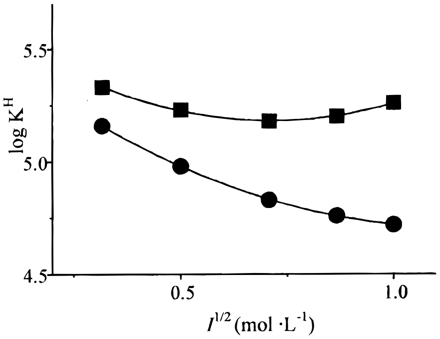

Figure 2. Protonation constants of polyacrylate anion (PAA) as a function of ionic strength (I) in Et_4NI (■) and NaCl (●) ($\alpha = 0.5$, $T = 25$ °C).

$[A^-]$ = free concentration of the deprotonated polyelectrolyte, and $[HA] + [A^-]$ = analytical concentration. In Table 2 log K^H values of protonation constants as function of α and I are reported. By observing these data, the following considerations can be made.

(i) Values of log K^H are a monotone increasing function of α, which can be expressed as a second-degree polynomial equation. [Equation 1 is equivalent to a quadratic function, such as $\log K^H = a_2\,\alpha^2 + a_1\alpha + a_0$ with $\log K_1^H = a_2 + a_1 + a_0$; $\log K_0^H = a_0$; $\log K_m^H = a_1 + 2a_0$. Alternatively, the equation $\log K^H = \log K_1^H\,\alpha + \log K_0^H\,\alpha\,(1 - \alpha) + B\alpha(1 - \alpha)$, can be used, with $B = 2 \log K_m^H - \log K_1^H - \log K_0^H$.]

(ii) Moreover, very different values are obtained in different background salts, and these differences increase with α; the trend is $Et_4NI > Me_4NCl > MNO_3 \cong MCl$ (with M^+ = alkali metal ions). Two examples of these trends are shown in Figures 1 and 2.

Data from Table 2 were fitted, using eq 1 to calculate the parameters K_1^H, and K_0^H, K_m^H, which are reported in Table 3, for some ionic strengths, together with $\bar{K}^H$ from eq 2. As expected, the trend of the three log K^H values is the same as that shown by log $\bar{K}^H$, as concerns their dependence on I. As an example, in Figure 3 we report log K_1^H vs $I^{1/2}$ in Et_4NI and NaCl. In terms of both dependence on I and differences between values in Et_4NI and NaCl, the behavior is, qualitatively, the same as that shown by low molecular weight polycarboxylic ligands (Daniele et al., 1985; De Robertis et al., 1999).

Dependence on Ionic Strength. The dependence on ionic strength of log K_1^H, log K_0^H, log K_m^H, and log $\bar{K}^H$, in the various background salts can be expressed by the polynomial equation

$$\log K^H = \log {}^TK^H + a_1 I^{1/2} + a_2 I + a_3 I^{3/2} \qquad (3)$$

Table 3. Some Smoothed Values for the Parameters of Eq 6 at Different Ionic Strengths, at $T = 25$ °C (See Also Supporting Information), for Polyacrylate Anion

salt	I/mol L^{-1}	log K_0^H	log K_1^H	log K_m^H	log $\bar{K}^H$
LiCl	0.1	4.50 ± 0.03[a]	6.11 ± 0.04[a]	4.96 ± 0.03[a]	5.19 ± 0.03[a]
	0.5	4.40 ± 0.02	5.42 ± 0.03	4.63 ± 0.02	4.82 ± 0.03
	1.0	4.38 ± 0.01	5.11 ± 0.02	4.38 ± 0.02	4.66 ± 0.02
	2.0	4.47 ± 0.01	5.12 ± 0.02	4.47 ± 0.02	4.68 ± 0.02
NaCl	0.1	4.51 ± 0.02	6.18 ± 0.04	4.98 ± 0.03	5.22 ± 0.03
	0.5	4.41 ± 0.01	5.64 ± 0.03	4.65 ± 0.03	4.90 ± 0.02
	1.0	4.37 ± 0.01	5.44 ± 0.02	4.54 ± 0.02	4.78 ± 0.02
	2.0	4.41 ± 0.01	5.35 ± 0.02	4.53 ± 0.02	4.76 ± 0.02
	3.0	4.53 ± 0.03	5.31 ± 0.02	4.63 ± 0.03	4.82 ± 0.03
KCl	0.1	4.50 ± 0.03	6.18 ± 0.04	4.98 ± 0.03	5.22 ± 0.03
	0.5	4.38 ± 0.02	5.64 ± 0.03	4.66 ± 0.02	4.89 ± 0.02
	1.0	4.32 ± 0.02	5.46 ± 0.02	4.55 ± 0.02	4.78 ± 0.02
	2.0	4.33 ± 0.02	5.41 ± 0.03	4.60 ± 0.02	4.78 ± 0.02
$LiNO_3$	0.1	4.50 ± 0.02	6.10 ± 0.03	4.96 ± 0.02	5.19 ± 0.02
	0.5	4.38 ± 0.02	5.40 ± 0.02	4.63 ± 0.01	4.80 ± 0.02
	1.0	4.32 ± 0.02	5.05 ± 0.03	4.38 ± 0.02	4.62 ± 0.02
$NaNO_3$	0.1	4.51 ± 0.03	6.18 ± 0.04	4.98 ± 0.03	5.22 ± 0.03
	0.5	4.41 ± 0.02	5.63 ± 0.03	4.66 ± 0.02	4.90 ± 0.02
	1.0	4.37 ± 0.01	5.42 ± 0.03	4.55 ± 0.02	4.78 ± 0.02
Me_4NCl	0.1	4.51 ± 0.04	6.50 ± 0.05	4.95 ± 0.04	5.32 ± 0.04
	0.5	4.43 ± 0.03	6.12 ± 0.04	4.67 ± 0.03	5.07 ± 0.03
	1.0	4.44 ± 0.04	5.98 ± 0.05	4.64 ± 0.04	5.02 ± 0.04
Et_4NI	0.1	4.57 ± 0.04	6.73 ± 0.05	4.98 ± 0.04	5.43 ± 0.04
	0.5	4.57 ± 0.04	6.46 ± 0.04	4.82 ± 0.03	5.28 ± 0.03
	1.0	4.78 ± 0.04	6.48 ± 0.05	4.89 ± 0.04	5.38 ± 0.04

[a] ±3s (s = std dev).

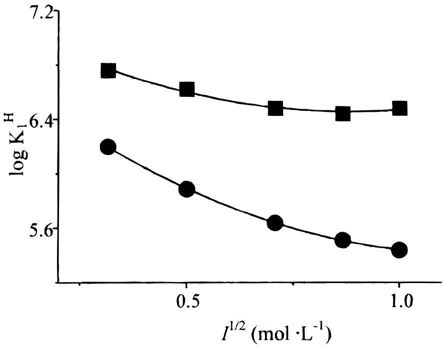

Figure 3. Protonation constants of polyacrylate anion (PAA) as a function of ionic strength (I) in Et_4NI (■) and NaCl (●), at $T = 25$ °C.

where K is the generic parameter of eq 2, ${}^TK$ is the parameter at zero ionic strength, and a_1, a_2, and a_3 are empirical fitting parameters. The values of a_i are reported in Table 4. In general, two terms of eq 3 are sufficient to fit log K vs I, except for values in NaCl ($I > 2$ mol L^{-1}). Values extrapolated to zero ionic strength are (±3 std dev)

$$\log {}^TK_0^H = 4.65 \pm 0.02$$

$$\log {}^TK_1^H = 6.95 \pm 0.10$$

$$\log {}^TK_m^H = 5.43 \pm 0.03$$

$$\log {}^T\bar{K}^H = 5.68$$

Dependence on Temperature of Protonation Constants. Potentiometric measurements were also performed at different temperatures, 15 ≤ T/°C ≤ 55, in NaCl (0.1 ≤ I/mol L^{-1} ≤ 1.0). The parameters of eq 1 are reported in Table 5, at each temperature and ionic strength. These values can be expressed as a function of t and I using the

Table 4. Parameters for Ionic Strength Dependence of Protonation Constants of Polyacrylate Anion, According to Eq 3

	a_1				a_2			
	$\log K_0^{H}$	$\log K_1^{H}$	$\log K_m^{H}$	$\log \bar{K}^{H}$	$\log K_0^{H}$	$\log K_1^{H}$	$\log K_m^{H}$	$\log \bar{K}^{H}$
NaCl	−0.48	−3.00	−1.70	−1.74	0.14	1.92	0.92	1.01
					0.05[a]	−0.42[b]	−0.12[c]	−0.17[d]
LiCl	−0.58	−3.06	−1.72	−1.76	0.32	1.25	0.73	0.75
KCl	−0.55	−2.62	−1.60	−1.60	0.23	1.09	0.72	0.68
$LiNO_3$	−0.53	−2.98	−1.53	−1.74	0.20	1.09	0.48	0.68
$NaNO_3$	−0.50	−2.78	−1.64	−1.66	0.22	1.25	0.76	0.76
Me_4NCl	−0.55	−2.98	−1.81	−1.36	0.34	2.97	1.03	0.70
Et_4NI	−0.55	−0.99	−1.75	−1.10	0.68	0.51	1.21	0.80

[a] a_3, $\log K_0$H. [b] a_3, $\log K_1$H. [c] a_3, $\log K_m$H. [d] a_3, $\log \bar{K}^{H}$.

Table 5. Parameters of Eq 1 at Different Temperatures and Ionic Strengths (NaCl), for Polyacrylate Anion

T/°C	I/mol L^{-1}	$\log K_0^{H}$	$\log K_1^{H}$	$\log K_m^{H}$
15	0.10	4.51[a]	6.14[b]	4.92[c]
15	0.25	4.46	5.84	4.72
15	0.50	4.41	5.60	4.58
15	1.00	4.39	5.43	4.50
25	0.10	4.52	6.22	4.94
25	0.25	4.47	5.90	4.73
25	0.50	4.42	5.63	4.58
25	1.00	4.39	5.43	4.48
35	0.10	4.54	6.31	4.97
35	0.25	4.48	5.98	4.76
35	0.50	4.44	5.69	4.59
35	1.00	4.40	5.44	4.47
45	0.10	4.56	6.42	5.00
45	0.25	4.50	6.08	4.79
45	0.50	4.45	5.77	4.60
45	1.00	4.41	5.47	4.46
55	0.10	4.58	6.55	5.05
55	0.25	4.52	6.19	4.83
55	0.50	4.47	5.86	4.63
55	1.00	4.42	5.52	4.47

[a] $3s(\log K_0^{H}) = 0.01-0.03$. [b] $3s(\log K_1^{H}) = 0.02-0.03$. [c] $3s(\log K_m^{H}) = 0.01-0.03$.

Table 6. Parameters for Dependence on Temperature[a] and Ionic Strength of Protonation Constants of Polyacrylate Anion in NaCl Aqueous Solution

	X_0	X_1	X_m	$\bar{X}$
ΔH°_{25}	2.7	15.9	4.7	7.8
$\Delta C^\circ_{p,25}$	67	460	215	247
a_1	−0.468	−2.68	−1.83	−1.66
a_2	0.211	1.16	0.882	0.751
a_2'	−0.00010	−0.00895	−0.00454	−0.00483

[a] ΔH° in kJ mol^{-1}; ΔC°_p in J K^{-1} mol^{-1}; X = generic parameter of eq 1.

Table 7. Protonation Constants of Acrylate Anion at Different Temperatures and Ionic Strengths in Et_4NI

T/°C	I/mol L^{-1}	$\log K^{H}$
15	0.10	4.07[a]
15	0.25	4.05
15	0.50	4.09
15	1.00	4.24
25	0.10	4.08
25	0.25	4.06
25	0.50	4.10
25	1.00	4.25
35	0.10	4.10
35	0.25	4.08
35	0.50	4.12
35	1.00	4.27
45	0.10	4.12
45	0.25	4.10
45	0.50	4.14
45	1.00	4.29
55	0.10	4.15
55	0.25	4.13
55	0.50	4.17
55	1.00	4.32

[a] $3s = 0.01-0.03$ (s = std dev).

equation

$$\log K = \log {}^{T}K_{25} + \Delta H^\circ_{25} F_1(T) + \Delta C^\circ_{p,25} F_2(T) + a_1 I^{1/2} + a_2 I + a_2' I(t - 25) \quad (4)$$

$$F_1(T) = [(1/\Theta) - (1/T)]\,(R \ln 10)^{-1}$$

$$F_2(T) = [(\Theta/T) - \ln(T/\Theta - 1)](R \ln 10)^{-1}$$

(a_1, a_2, and a_2' are empirical parameters; T = absolute temperature/K; Θ = reference temperature/K, in this work 298.15 K). In Table 6 we report the calculated parameters of eq 4. ΔH° values for protonation reaction are consistent with those reported for low molecular weight ligands. The order $\Delta H^\circ_0 < \Delta H^\circ_m < \Delta H^\circ_1$ is the same as for polycarboxylic acids. For example, for the four protonation steps of 1,2,3,4-butanetetracarboxylic acid (De Robertis et al., 1999), we found a similar decreasing trend: $\Delta H^\circ_1 = 6.7$, $\Delta H^\circ_2 = -0.8$, $\Delta H^\circ_3 = -1.1$, and $\Delta H^\circ_4 = -3.8$ kJ mol^{-1}. ΔC°_p values are affected by large errors (~ ±100 J K^{-1} mol^{-1}), but they are in accordance with the general trend of carboxylic acids (De Robertis et al., 1999, and references reported therein).

Protonation of Acrylate Anion. To compare thermodynamic parameters of poly(acrylic acid) with those of the monomeric species, potentiometric measurements were performed in solution, at different temperatures, $15 \le T/°C \le 45$, and ionic strengths, $0.1 \le I/\text{mol L}^{-1} \le 1.0$, in Et_4NI containing acrylic acid. Protonation constants at different temperatures and ionic strengths are reported in Table 7. By using the equation:

$$\log K^{H} = \log {}^{T}K^{H} + \Delta H^\circ_{25} F_1(T) + \Delta C^\circ_{p,25} F_2(T) - 2I^{1/2}(2 + 3I^{1/2})^{-1} + CI + DI^{3/2} \quad (4a)$$

to fit the data in Table 6, we obtained (±3 std dev)

$$\log {}^{T}K^{H} = 4.258 \pm 0.015$$

$$\Delta G^\circ = -24.3 \pm 0.1 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = 2.4 \pm 0.6 \text{ kJ mol}^{-1}$$

$$T\Delta S^\circ = 26.7 \pm 0.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta C^\circ_p = 125 \pm 75 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C = 0.334$$

$$D = -0.058$$

The value of $\log {}^{T}K^{H}$ is fairly close to $\log {}^{T}K_0^{H}$ of polyacrylate, while ΔH°, taking into account the error, is in practice coincident.

Table 8. Formation Constants for Alkali Metal Complexes of Polyacrylate Anion, at Different Ionic Strengths, at $T = 25$ °C

	I/mol L^{-1}	$\log K_1^{M}$	$\log \bar{K}^{M}$
Li	0.10	1.50 ± 0.12^{a}	0.87 ± 0.11^{a}
	0.50	1.30 ± 0.11	0.58 ± 0.07
	1.00	1.35 ± 0.10	0.63 ± 0.06
	0	2.01 ± 0.10	1.37 ± 0.07
		$b_1 = 1.35^{b}$	$b_1 = 1.25$
Na	0.10	1.41 ± 0.11	0.79 ± 0.10
	0.50	1.05 ± 0.11	0.45 ± 0.08
	1.00	1.00 ± 0.11	0.47 ± 0.07
	0	1.93 ± 0.12	1.30 ± 0.08
		$b_1 = 1.06$	$b_1 = 1.17$
K	0.10	1.41 ± 0.13	0.79 ± 0.12
	0.50	1.05 ± 0.12	0.46 ± 0.08
	1.00	0.98 ± 0.11	0.47 ± 0.07
	0	1.94 ± 0.11	1.30 ± 0.07
		$b_1 = 1.04$	$b_1 = 1.17$

[a] ±3(std dev). [b] b_1 = parameter of eq 6.

$Na^{+}-K^{+}-Li^{+}$ Complexes. To evaluate the extent of interaction of the polyacrylate ligand with alkaline metal ions, a complexation model, where all possible interactions ($K > 0.1$ mol L^{-1}) between the components of the system under study are taken into account, has been applied. The model has been well tested for several systems (Daniele et al., 1985; De Robertis et al., 1993; De Stefano et al., 1994). In particular, for carboxylate systems the following hypotheses must be considered: (a) carboxylic groups form weak complexes with alkali metal ions; (b) tetraethylammonium salts (iodide or bromide) do not significantly interact with carboxylic ligands and the protonation data in Et_4NI can be considered as a baseline (Daniele et al., 1985; De Robertis et al., 1993). On the basis of these assumptions, all the deviation (lowering) from the protonation constants values determined in tetraethylammonium iodide can be interpreted in terms of species formation $M^{+}-PAA$ (where $M^{+} = Na^{+}, Li^{+}, K^{+}$) and the formation constants can be calculated by using a simple equation:

$$\Delta\log K^{H} = \log K^{H}_{\text{baseline}} - \log K_{M}^{H} = \log(1 + K^{M}[M^{+}]) \tag{5}$$

where $\log K_{M}^{H}$ is the protonation constant of polyacrylate anion in alkali metal chlorides, $\log K^{H}_{\text{baseline}}$ is the protonation constant in Et_4NI, and K^{M} is the formation constant of the species M−PAA (M^{+} = sodium, potassium, and litium). Calculations were performed using $\log K_1^{H}$ values in eq 5, obtained using the formation constant involving a fully deprotonated polyelectrolyte ($\alpha \rightarrow 1$). If we use the $\log \bar{K}^{H}$ parameter in eq 5, we may calculate $\log \bar{K}^{M}$, which can be considered a thermodynamic formation constant for $0 < \alpha < 1$. Both formation constant values are reported in Table 8 at different ionic strengths. The dependence on ionic strength of $\log K_1^{M}$ (Li^{+}, Na^{+}) is shown in Figure 4. The equation

$$\log K^{M} = \log {}^{T}K^{M} - 2I^{1/2} + b_1 I \tag{6}$$

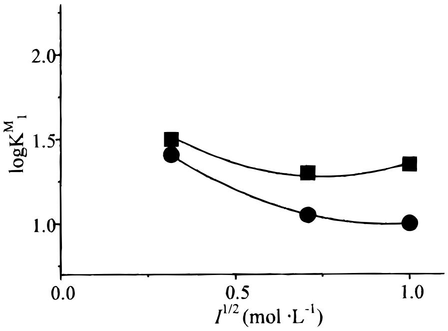

Figure 4. Formation constants of polyacrylate anion (PAA) as a function of ionic strength (I) in NaCl (■) and LiCl (●), at $T = 25$ °C.

can be used to express both $\log K_1^{M}$ and $\log \bar{K}^{M}$ as a function of I. Formation constants extrapolated to zero ionic strength and empirical parameters b_1 are reported in Table 8 [the standard deviation on the fit of eq 6 is $\sigma = 0.017$].

Thermodynamic Parameters for the Protonation of Polyacrylate. Protonation data at different temperatures (Table 5) can be interpreted in terms of $\Delta H°$ contribution for each parameter of eq 1 (Table 6). All the thermodynamic parameters (at constant pressure) are reported in Table 4. Calculated $\Delta H°$, $T\Delta S°$, and $\Delta C°_p$ are of the same order of magnitude as those of low molecular weight polycarboxylic ligands (De Robertis et al., 1999), and moreover $T\Delta S°$ vs $\Delta G°$ is a linear function as predicted by Bjerrum theory (King, 1965). Note that, though $\Delta C°_p$ is affected by quite a large error, the value for the mean protonation parameter ($\Delta C°_p = 247$ J K^{-1} mol^{-1}) is quite close to the mean value found for low molecular weight polycarboxylic acids ($\Delta C°_p = 230$ J K^{-1} mol^{-1}) (De Robertis et al., 1999).

Final Remarks

In this work we have reported a large amount of protonation data for polyacrylate anion (MW = 2000 Da), in seven ionic media at different ionic strengths, and for one background salt (NaCl) also at different temperatures. For comparison, data are also reported for the protonation of acrylate anion at different temperatures and ionic strengths (Et_4NI). Protonation constants calculated at each α value can be expressed by three parameters (eq 1). This equation is quite useful in reducing the amount of protonation data, and, moreover allows handling of thermodynamic parameters for proton equilibria of polyelectrolytes as well as for low molecular weight anions. The trend for $\log K^{H}$, $Et_4N^{+} > Me_4N^{+} > Li^{+} > Na^{+} \sim K^{+}$, and the dependence of parameters of eq 1 are comparable to those shown by simple polycarboxylic anions, such as 1,2,3-propanetricarboxylic and 1,2,3,4-butanetetracarboxylic acids. Poly(acrylic acid) binds alkali metal cations, in particular when the polyanion is fully deprotonated (at pH = 8, ~80% of the ligand is complexed by Na^{+}, in the presence of 0.5 mol L^{-1} NaCl). From data at different temperatures it was possible to obtain $\Delta H°$ protonation values, for each parameter of eq 1, together with $\Delta G°$ and $\Delta S°$. These are the first thermodynamic data reported to

Table 9. Thermodynamic Parameters for the Protonation of Polyacrylate Anion, at $T = 25$ °C

	$-\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})	$T\Delta S°$ (kJ mol^{-1})	$\Delta C°_p$ (J K^{-1} mol^{-1})
X_0	26.5 ± 0.3^{a}	2.7 ± 0.6^{a}	98 ± 3^{a}	29 ± 1^{a}	67^{b}
X_1	39.6 ± 0.6	15.9 ± 1.8	186 ± 5	56 ± 2	460
X_m	31.0 ± 0.3	4.7 ± 0.5	120 ± 3	36 ± 1	214
X	32.4 ± 0.3	7.8 ± 0.7	135 ± 3	40 ± 1	247

[a] ±3(std dev). [b] ±30−50%.

date for poly(acrylic acid). A comparison of the thermodynamic parameters for protonation of the monomer (acrylate anion) and protonation of polyacrylate anion at $\alpha \rightarrow 0$ reveals that the difference in $\Delta G°$ values (2.2 kJ mol^{-1}) is entirely due to the differences in $T\Delta S°$ (2 kJ mol^{-1}).

Supporting Information Available:

Apparent protonation constants of polyacrylate anion (PAA) as a function of ionic strength, in different ionic media (LiCl, $LiNO_3$, NaCl, $NaNO_3$, KCl, Me_4NCl, Et_4NI) at $T = 25$ °C are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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