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Sequestration of organometallic compounds by natural organic matter. binding of trimethyltin(IV) by fulvic and alginic acids

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The binding capacity of fulvic and alginic acids towards trimethyl tin(IV) cation was quantitatively determined in order to evaluate the sequestering ability of toxic organometallic compounds by natural organic matter. Investigations were performed in the pH range of natural waters (5–8.5) where the carboxylate groups, largely present in both sequestering agents, are the main binding sites. A chemical interaction model, according to which both the protonation of polyelectrolyte ligands and the hydrolysis of the organotin cation in NaCl aqueous solution were considered, was used to define the speciation of the systems under investigation. Measurements performed at different ionic strength values (0.1, 0.25, 0.5 and 0.7 mol L^{-1}, NaCl) allowed us to consider the dependence of stability constants on the ionic strength, and to calculate the formation constants at infinite dilution. Results obtained show the formation of the complex species TMT(L), $TMT(L)_2$ and TMT(L)(OH) for L = fulvic acid and TMT(L) for L = alginic acid, respectively. In order to compare the strength of interaction of these natural poly electrolytes with other analogous synthetic polyelectrolytes, measurements were also carried out on the trimethyltin(IV)–polyacrylate (5.1 kDa) system, and in this case the formation of TMT(L), $TMT(L)_2$ and TMT(L)(OH) species was found. Results show the following trend of stability for the species TMT(L) in the systems investigated: TMT–fulvate $\approx$ TMT–polyacrylate > TMT–alginate. On the basis of the stability data obtained, the lowest concentration of fulvic and alginic acids, able to act as sequestering agents towards triorganotin(IV) cation in the conditions of natural waters, was also calculated. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: natural organic matter; organometallic compounds; sequestration; complexation; speciation

INTRODUCTION

Aqueous solution chemistry of organotin(IV) compounds has been extensively investigated during recent years with the aim of defining their chemical speciation in natural waters. Several studies have been carried out on the hydrolysis processes of organotin cations in different aqueous media, also simulating the composition of natural waters, and at different ionic strength values.[1–9] The association of organotin(IV) cations with ligands of biological and environmental interest was also investigated by different authors,[10–12] and many data have been reported recently[13] on the organotin complexes with biologically active ligands. In these ligands, the ions and molecules containing carboxylic groups are by far the most common naturally occurring binding sites for metal ions and organometallic cations. During recent years we carried out a systematic study on mono-, di- and triorganotin carboxylate complex formation.[14–18] To add a further contribution to the knowledge of the speciation of triorganotin compounds,

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whose toxicity towards mammals and aquatic organisms is well recognized,[19–22] we extended our investigations to their interaction with naturally occurring high molecular weight carboxylic ligands. In this light, we studied the association of trimethyltin (TMT) cation with fulvic and alginic acids (FA and AA, respectively), which are important components of living (AA is one of the main components of brown algae) and nonliving natural organic matter in aquatic ecosystems. It is well known that fulvic acids represent the most soluble fraction of humic substances and are very rich in carboxylic groups.[23–26] These binding sites allow fulvic acid to interact with metal ions, playing a key role in metal removal and/or transport in soils and aquatic ecosystems. A generic hypothetical structure containing carboxylic groups in both aromatic and alkyl linear chains, is shown in Fig. 1.

Alginic acid is one of the main components of brown algae and it is a co-polymer of 1,4 linked β-D-mannuronic (M) and α-L-guluronic (G) acid residues, each containing one carboxylate group per monomeric unit[27] (Fig. 2). The metal biosorption by algal biomass has been well known for many years[28–32] and it is established that metal uptake occurs by carboxyl binding sites of saccharide components of marine algae.[33–36] The interest in metal biosorption process has increased in recent years to provide a low-cost technology for soil remediation and wastewater treatment.[37,38]

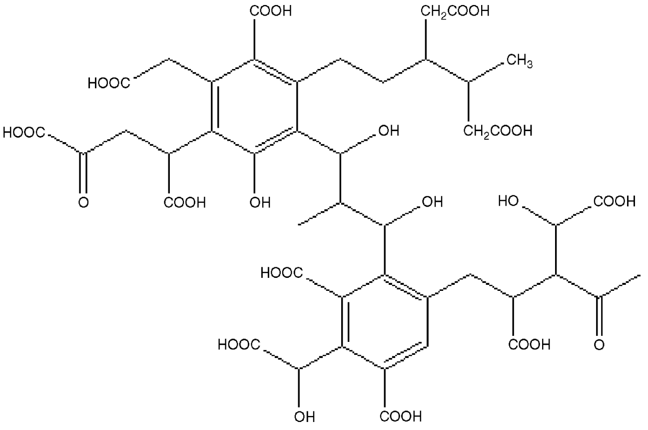

Figure 1. Hypothetical generic structure of fulvic acid.

The adsorption/release processes of organotin compounds in sediments have been widely investigated, in particular to evaluate the toxicity of tributhyltin towards biota.[39–42] In spite of that, very little data has been reported in the literature on the association of triorganotin (TOT) compounds with natural organic matter,[43,44] and they refer mainly to the humic substances. No quantitative data has been reported on the stability of species formed in both TOT–FA and TOT–AA systems. This is probably due to the difficulty of defining exactly the acid–base behaviour of these polyelectrolytes ligands, i.e. the effective charge of the polyanions in the different pH ranges. A chemical model based on the dependence of protonation constants on the dissociation degree of the polyelectrolyte under investigation allowed us to determine the proton exchange capacity of both fulvic and alginic acids in different ionic media and at different ionic strengths. The results, reported in recent papers,[45,46] are used here to determine the formation constants of complex species in the systems under investigation. Details of the chemical model for the binding capacity of poly-carboxylate ligands are reported in the section on the association chemical model.

To evaluate the sequestering capacity of TOT compounds by the cited ligands, we chose trimethyltin(IV) for the main following reasons: (i) among trialkyltin(IV) compounds, trimethyltin derivatives are recognized as the most toxic towards mammals;[20,47] (ii) the high solubility of trimethyltin compounds allows potentiometric measurements to be carried out, which cannot be performed using tributyltin owing to its very low solubility; (iii) a comparative study on the hydrolysis of trimethyl, triethyl and tripropyltin(IV) cations[8] allowed us to find a relationship to predict the acid–base behaviour of tributyltin, which is very similar to that of trimethyltin. This confirms the possibility of using TMT as a representative of trialkyltin derivatives.

Experimental measurements on TMT–FA and TMT–AA systems were performed using a potentiometric technique

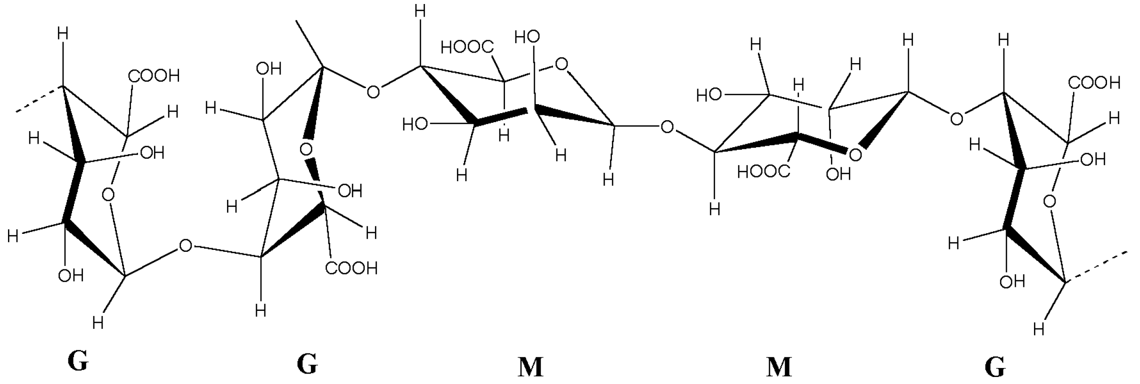

Figure 2. Structure of alginic acid (G = guluronic acid; M = mannuronic acid).

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([H^+]-glass electrode) at $t = 25\,°C$, in NaCl ionic medium and at different ionic strengths (0.1, 0.25, 0.5 and 0.7 mol L^{-1}). Additional measurements were performed on the TMT–polyacrylate system (polyacrylic acid, PAA, 5.1 kDa) to compare the results obtained using naturally occurring and synthetic polycarboxylate ligands. Investigations were performed in the pH range (5–8.5) of interest for natural waters. Since natural aquatic systems show a large range of ionic strength values (from ~0.07 mol L^{-1}, or less, for fresh waters to 0.7 mol L^{-1}, or more, for sea waters), the dependence of formation constants on ionic strength was also studied. To this end a Debye Hückel-type equation was used, which allowed to calculate the thermodynamic formation constants and the parameters for the ionic strength dependence for all the complex species formed.

EXPERIMENTAL

Materials

Trimethyltin(IV) cation was used as chloride salt (Aldrich product). Standard fulvic acid was supplied by the International Humic Substances Society IHSS (lot no. 2S102F) with a water and ash content of 11.2 and 1.0%, respectively, and with the following elemental composition: 50.12 (C%), 4.28 (H%), 42.61 (O%), 3.75 (N%), 0.89 (S%) and 0.12 (P%). The content of carboxylic groups in fulvic acid (meq mg^{-1}) was checked in our laboratories by potentiometric technique and also using the classical calcium acetate method to determine functional groups in humic substances.[25,48] Commercial alginic acid from *Macrocystis pyrifera* was supplied by Aldrich with an average content of mannuronic (M) and guluronic (G) acids of 61 and 39%, respectively, with an M:G ratio of 1.56. Polyacrylic acid (5.1 kDa) was supplied by Fluka with an average water content of 26%. Its purity, checked by potentiometric titrations, was always >99.5%. Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated Fluka ampoules and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. NaCl (Fluka) was used after drying in stove at 140 °C. All the solutions were prepared using freshly prepared CO_2-free ultrapure water (R = 18 MΩ) and grade A glassware.

Procedure

Potentiometric titrations were carried out (at 25.0 ± 0.1 °C) using an apparatus consisting of a model 713 Metrohm potentiometer, equipped with a combined glass electrode (Ross type 8102, from Orion) and a model 765 Metrohm motorized burette. The estimated accuracy was ±0.15 mV and ±0.003 mL for e.m.f. and titrant volume readings, respectively. The apparatus was connected to a PC, and automatic titrations were performed using a home-made computer program to control titrant delivery and data acquisition and to check for e.m.f. stability. All titrations were carried out under magnetic stirring and presaturated N_2 was bubbled through the solution in order to exclude O_2 and CO_2 inside. The solutions under investigation consisted of known amounts of fulvic or alginic acids (1–1.5 mmol L^{-1}) or polyacrylate (6–12 mmol L^{-1}) and trimethyltin(IV) chloride (0.5–1 mmol L^{-1} in the fulvate and alginate systems; 3–7 mmol L^{-1} in the polyacrylate system). Different amounts of sodium chloride were added in turn to obtain pre-established ionic strength values ($I = 0.1$, 0.25, 0.5 and 0.7 mol L^{-1}). Alginic acid was used as sodium salt obtained by adding NaOH to the acidic solution up to pH ~9. Titrations in the AA–TMT–NaCl system were carried out from alkaline to acidic pH values with standard hydrochloric acid solutions. Metal to ligand ratios in the titrand solutions were always $1:1 \leq \mathrm{TMT}:\mathrm{L} \leq 1:2$ (L = AA, FA or PAA 5.1 kDa). Details on the experimental conditions are given in Table 1. Potentiometric measurements were carried out by titrating 25 mL of the solution under investigation with standard NaOH (for FA–TMT and PAA–TMT systems) or HCl (for AA–TMT system) solutions. For each experiment, independent titrations of HCl solutions were performed with standard sodium hydroxide solutions in the same experimental conditions of ionic strength and temperature as the systems under investigation to determine the formal electrode potential.

Calculations

The following computer programs[49] were used in the calculations: (i) BSTAC and STACO for the refinement of all the parameters of an acid-base titration (E^0, pK_w, coefficient of junction potential j_a, analytical concentration of reagents) and for the calculation of complex formation constants; (ii) ES4ECI to draw speciation diagrams and compute species formation percentages; (iii) LIANA to test the dependence of $\log \beta$ on ionic strength. Formation constants, concentrations and ionic strengths are expressed in the molar (mol L^{-1}) concentration scale. The dependence of formation constants on ionic strength was taken into account using the following Debye–Hückel type equation (1), already proposed in different forms by our research group,[50,51] and also recently used in modelling of natural and synthetic polyelectrolyte interactions in natural waters:[45]

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

with

$$z^{*} = \Sigma\ (\text{charges})^{2}{}_{\text{reactants}} - \Sigma\ (\text{charges})^{2}{}_{\text{products}} \qquad (1a)$$

where β is the formation constant and ${}^{T}\beta$ is the formation constant at infinite dilution. C is an empirical parameter.

THE ASSOCIATION CHEMICAL MODEL

Equilibria involved in the association of trimethyltin(IV) cation with polyelectrolyte ligands are:

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Table 1. Experimental conditions for measurements in TMT–FA, TMT–AA and TMT–PAA systems in $NaCl_{aq}$, at $t = 25\,^{\circ}C$

$I(\text{mol L}^{-1})^a$	$C_{TMT}(\text{mol L}^{-1})$	$C_L(\text{mol L}^{-1})$	$C_H(\text{mol L}^{-1})$	pH range	Runs	Total number of points
TMT–FA						
0.002	0.00099	0.001250	0.001250	5.27–8.10	3	157
0.002	0.00100	0.001270	0.001270	5.10–7.59	2	112
0.091	0.00099	0.001250	0.001250	5.24–8.09	4	208
0.228	0.00100	0.001270	0.001270	5.05–8.17	3	177
0.452	0.00101	0.001007	0.001007	5.49–8.09	3	159
0.623	0.00095	0.001270	0.001270	5.26–8.08	3	164
0.628	0.00067	0.001400	0.001400	5.32–8.29	2	102
TMT–AA						
0.001	0.000480	0.001000	0.000662	6.06–8.60	2	68
0.001	0.000480	0.001000	0.000705	6.03–7.99	1	28
0.001	0.000476	0.000998	0.001087	6.03–8.37	2	61
0.104	0.000480	0.001000	0.000662	6.06–8.60	2	66
0.103	0.000480	0.001000	0.000705	6.03–7.99	1	25
0.106	0.000480	0.001010	0.000512	6.13–7.80	1	26
0.100	0.000476	0.000998	0.001087	6.05–8.37	1	28
0.103	0.000478	0.001004	0.000802	6.00–8.25	1	29
0.102	0.000476	0.001003	0.000872	5.94–8.71	1	28
0.254	0.000486	0.001064	0.000532	6.03–8.60	3	87
0.253	0.000486	0.001015	0.000581	5.94–8.52	3	82
0.496	0.000486	0.001010	0.000585	5.93–8.64	4	125
0.505	0.000486	0.001025	0.000570	6.00–8.45	3	95
0.687	0.000482	0.000957	0.000609	5.92–8.62	3	93
0.688	0.000486	0.000981	0.000615	6.04–8.51	3	94
TMT–PAA, 5.1 kDa						
0.514	0.006774	0.012313	0.012000	5.08–7.45	1	47
0.513	0.008326	0.012263	0.012000	4.92–7.46	1	48
0.510	0.003699	0.009071	0.010000	5.18–6.98	1	32
0.501	0.004888	0.006997	0.010000	5.11–7.32	1	32
0.505	0.003217	0.006263	0.007000	5.15–7.25	1	29

[a] Effective ionic strength (mean value of the runs).

(1) Polyelectrolyte protonation equilibria:

$$L^{z-} + nH^+ = LH_n{}^{(n-z)} \tag{2}$$

(2) Trimethyltin(IV) cation hydrolysis:

$$(CH_3)_3Sn^+ + H_2O = (CH_3)_3Sn(OH)^0 + H^+ \tag{3}$$

$$(CH_3)_3Sn(OH)^0 + H_2O = (CH_3)_3Sn(OH)_2{}^- + H^+ \tag{3a}$$

(3) Complex formation equilibria:

$$(CH_3)_3Sn^+ + nL^{z-} = (CH_3)_3Sn(L)_n{}^{(1-nz)} \tag{4}$$

$$(CH_3)_3Sn(OH)^0 + L^{z-} = (CH_3)_3Sn(OH)(L)^{z-} \tag{5}$$

where L is the polyelectrolyte (fulvic, alginic or polyacrylic) ligand.

Protonation of polyelectrolytes

Equation 2 refers to the protonation equilibrium of a generic acidic polyelectrolyte whose protonation constants are strongly dependent on the dissociation degree of the polyelectrolyte, $\alpha = [L]/[H_nL]$. By taking into account the dependence on α of $\log K^H$, stoichiometric protonation constants for both fulvic and alginic acids were determined using two different equations. The first one is that proposed by Katchalsky[52,53] [equation (6)], derived from the Henderson–Hasselbalch equation

$$\log K^{H^*} = \log K^H{}_n - (n-1)\log[(1-\alpha)/\alpha] \tag{6}$$

The second one is a slightly more accurate equation (7), based on the zeroth approximation,[54] which was proposed by Högfeldt *et al.*[55]

$$\log K^H = \alpha^2 \log K_1^H + (1-\alpha)^2 \log K_0^H + 2\alpha(1-\alpha)\log K_m^H \tag{7}$$

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Table 2. Values of $\log K_1^{\mathrm{Ha}}$ of fulvic and alginic acids in $\mathrm{NaCl_{aq}}$ at different ionic strengths and at $t = 25\,^{\circ}\mathrm{C}$

Fulvic acid		Alginic acid	
I(mol $\mathrm{L^{-1}}$)	$\log K_1^{\mathrm{H}}$	I(mol $\mathrm{L^{-1}}$)	$\log K_1^{\mathrm{H}}$
0.1	5.63	0.1	3.61
0.25	5.19	0.25	3.44
0.5	4.99	0.5	3.23
0.75	4.80	1	3.16

[a] Values from refs. 34,35; $\log K_1^{\mathrm{H}}$ refers to equilibrium of equation (2).

where $\log K_1^{\mathrm{H}}$ is the protonation constant of the polyelectrolyte when $\alpha \to 1$; $\log K_0^{\mathrm{H}}$ is the protonation constant of the polyelectrolyte when $\alpha \to 0$; $\log K_{\mathrm{m}}^{\mathrm{H}}$ is the protonation constant of the polyelectrolyte in an intermediate value that takes into account the nonlinearity of the function $\log K^{\mathrm{H}}$ vs α. The values of the protonation constants of fulvic and alginic acids here used were previously determined in different ionic media at different ionic strengths.[45,46] Since the aim of this work is to define the sequestering capacity of fulvic and alginic acids towards trimethyltin(IV), i.e. the stability of the TMT-FA and TMT-AA complex species formed in the pH range of natural waters (5–8a), only the protonation constants of polyelectrolytes when $\alpha \to 1$ ($\log K_1^{\mathrm{H}}$) have been considered in the calculations. The effective charges of the polyions in these dissociation conditions are $z = -3.5$ and $z = -4$ for fulvate[34] and alginate,[34,35] respectively. The values of $\log K_1^{\mathrm{H}}$ of fulvic and alginic acids in NaCl medium used in this work are reported in Table 2. For polyacrylic acid we used $\log K_1^{\mathrm{H}} = 5.79$ ($\mathrm{I} = 0.5$ mol $\mathrm{L^{-1}}$ in $\mathrm{NaNO_3}$ ionic medium).[56]

Hydrolysis of trimethyltin

The hydrolysis of the trimethyltin(IV) cation [Equations (3) and (3a)] has been wholly defined, as well as the influence of ionic strength and medium on the values of the relative constants.[2,4,6,9] As shown in the references, the second hydrolysis step of the TMT cation [equation (3a)] occurs at pH over 9 and it will not be considered in this work. Table 3 shows the values of hydrolysis constants of TMT, in the ionic strength range from 0.1 to 0.75 mol $\mathrm{L^{-1}}$ (NaCl medium), which were always taken into account in the calculations to quantitatively determine the association of TMT with fulvic and alginic ligands in the same medium. In the same table the hydrolysis constant of TMT at infinite dilution ($I = 0$ mol $\mathrm{L^{-1}}$), calculated by the Debye Hückel type equation (1) for the dependence of formation constants on ionic strength, is also reported.

Table 3. Hydrolysis constants of $\mathrm{(CH_3)_3Sn^+}$ in $\mathrm{NaCl_{aq}}$ at different ionic strengths and at $t = 25\,^{\circ}\mathrm{C}$

I(mol $\mathrm{L^{-1}}$)	$-\log K_{1-1}$[a]
0.00	6.143
0.10	6.164
0.20	6.185
0.50	6.250
0.75	6.303

[a] Values from ref. 2; $\log K_{1-1}$ refers to equilibrium of equation (3).

RESULTS

Association of trimethyltin(IV) with fulvic and alginic ligands

By taking into account the association model above described, the binding of TMT by FA and AA was evaluated in the pH range 5–8.5, in correspondence to the wholly unprotonated polyelectrolytes. Calculations, carried out on the experimental potentiometric data by means of least squares computer programs, gave evidence for the formation of the following species: TMT(FA), $\mathrm{TMT(FA)_2}$ and TMT(FA)(OH) for trimethyltin–fulvate and TMT(AA) for trimethyltin–alginate systems. Tables 4 and 5 show the stability constants of the species formed in the two systems in NaCl medium at different ionic strength values.

The two natural ligands form, in the same experimental condition, different species with TMT cation. This behaviour can be easily explained by remembering that fulvic

Table 4. Formation constants of TMT–FA complex species[a] in $\mathrm{NaCl_{aq}}$ at different ionic strengths and at $t = 25\,^{\circ}\mathrm{C}$

I^{b} (mol $\mathrm{L^{-1}}$)	$\log \beta_{110}$	$\log \beta_{120}$	$\log \beta_{11-1}$
0.002	$5.46 \pm 0.01^{\mathrm{c}}$	$7.26 \pm 0.01^{\mathrm{c}}$	$-1.41 \pm 0.01^{\mathrm{c}}$
0.091	4.34 ± 0.03	7.99 ± 0.02	-1.73 ± 0.02
0.228	3.80 ± 0.03	7.23 ± 0.01	-2.32 ± 0.02
0.452	3.24 ± 0.07	6.37 ± 0.02	-3.06 ± 0.05
0.622	3.23 ± 0.07	5.75 ± 0.08	-3.37 ± 0.07

[a] Complexes species formation refers to the equilibrium: $p\mathrm{TMT^+} + q\mathrm{FA^{3.5-}} + r\mathrm{H_2O} = \mathrm{(TMT)}_p\mathrm{(FA)}_q\mathrm{(OH)}_r{}^{(p-3.5q-r)} + \mathrm{rH^+}$.
[b] Effective ionic strength.
[c] Standard deviation.

Table 5. Formation constants of TMT–AA complex species[a] in $\mathrm{NaCl_{aq}}$ at different ionic strengths and at $t = 25\,^{\circ}\mathrm{C}$

I^{b} (mol $\mathrm{L^{-1}}$)	$\log \beta_{110}$
0.001	$3.510 \pm 0.008^{\mathrm{c}}$
0.105	2.948 ± 0.007
0.251	2.564 ± 0.007
0.499	2.721 ± 0.005
0.687	2.790 ± 0.006

[a] Complexes species formation refers to the equilibrium $p\mathrm{TMT^+} + q\mathrm{AA^{4-}} + r\mathrm{H_2O} = \mathrm{(TMT)}_p\mathrm{(AA)}_q\mathrm{(OH)}_r{}^{(p-4q-r)} + \mathrm{rH^+}$.
[b] Effective ionic strength.
[c] Standard deviation.

acids contain more carboxylic groups than alginic acid ($\text{meq/g}_{(\text{fulvic acid})} > \text{meq/g}_{(\text{alginic acid})}$). As a consequence, the stability follows the trend FA > AA and, in turn, alginate is not able to bind a second carboxylate group. Moreover, at pH > 7.5, where TMT hydrolysis species formation is quite high, alginate cannot bind TMT in the hydrolysed form to give TMT(AA)(OH) species. These differences in complex species formation greatly influence the quantitative sequestration capacity of alginic and fulvic ligands towards triorganotin cations, as we will show later in this work.

Figures 3 and 4 show the dependence on ionic strength of formation constants for the species in the TMT–FA and TMT–AA systems, respectively, in NaCl ionic medium.

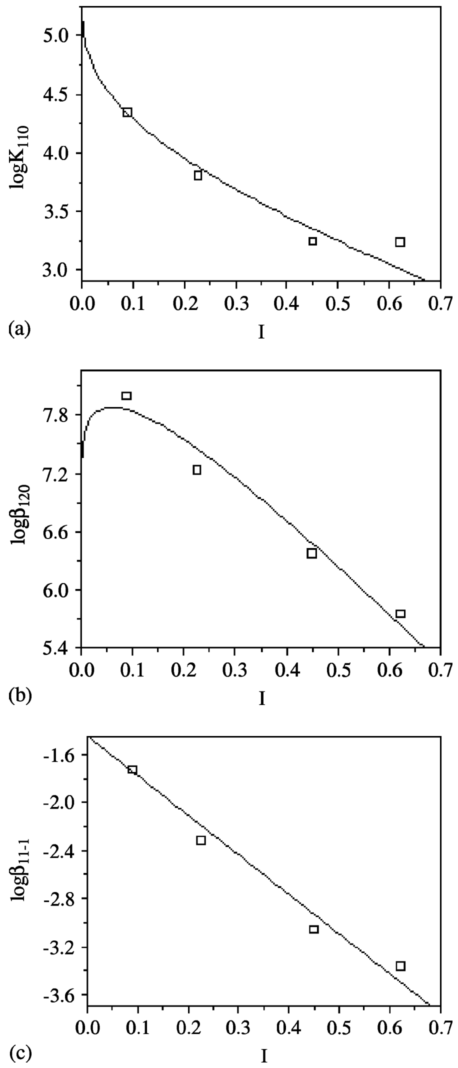

Figure 3. Dependence of formation constants on ionic strength for the TMT(FA) (a), TMT(FA)_2 (b) and TMT(FA)(OH) (c) complex species in NaCl_{aq}, at $t = 25\,^\circ\text{C}$.

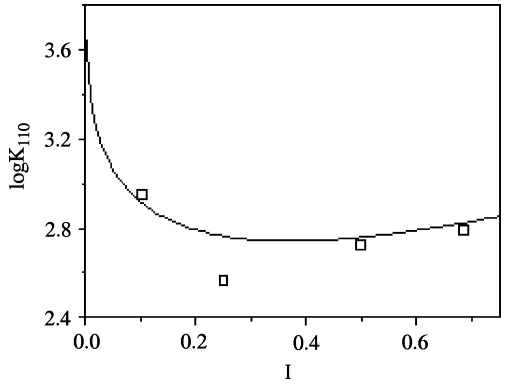

Figure 4. Dependence of formation constants on ionic strength for the TMT(AA) complex species in NaCl_{aq}, at $t = 25\,^\circ\text{C}$.

Table 6. Formation constants of TMT-L complexes (L = FA or AA ligand) at $I = 0\ \text{mol L}^{-1}$ and $t = 25\,^\circ\text{C}$, together with empirical parameters for the dependence on ionic strength [equation (1)]

pqr	$\log^{\text{T}} \beta_{pqr}$ [a]	*C*	σ [b]
	TMT–FA		
110	5.25 ± 0.1 [c]	-1.5 ± 0.3	0.1
120	7.26 ± 0.06	-5.7 ± 0.2	0.1
11-1	-1.45 ± 0.07	-3.3 ± 0.2	0.1
	TMT–AA		
110	3.7 ± 0.1	0.9 ± 0.1	0.06

[a] Complexes formation constants refer to equilibrium: $p(\text{TMT})^+ + q\text{L}^{z-} + r\text{H}_2\text{O} = (\text{TMT})_p\text{L}_q\text{OH}_r{}^{(p-zq-r)} + r\,\text{H}^+$.
[b] Standard deviation on the fit.
[c] Standard deviation on the parameters.

The dependence of formation constants ($\log \beta_{pqr}$) on ionic strength for the two systems investigated was defined by the Debye–Hückel type equation (1), as described in the Experimental section. The $\log^{\text{T}} \beta_{pqr}$ values at infinite dilution ($I = 0\ \text{mol L}^{-1}$) for species formed in the TMT–FA and TMT–AA systems, together with the empirical parameter *C* of the equation and standard deviations on the fit, are reported in Table 6.

In Tables 7 and 8 we report the calculated formation constant values obtained from the fit. As can be seen, the accordance between experimental and calculated data is quite satisfactory and indicates that the proposed model for the dependence on ionic strength is correct.

DISCUSSION

Speciation profiles

As it is clearly shown in the diagrams of Figure 5(a, b), the species distribution in the two systems investigated is very different depending on the speciation models above described. The most evident difference is due to the formation of the TMT(L)_2 and TMT(L)(OH) species which are present only in TMT–FA system with high

Table 7. Calculated values of formation constants of TMT–fulvate complex species in NaCl, at different ionic strengths and at $t = 25\,^\circ$C

I^a	$\log \beta_{110}{}^b$	$\lvert\Delta \log \beta_{\text{calcd-exp.}}\rvert$	$\log \beta_{120}{}^b$	$\lvert\Delta \log \beta_{\text{calcd-exp.}}\rvert$	$\log \beta_{11-1}{}^b$	$\lvert\Delta \log \beta_{\text{calcd-exp.}}\rvert$
0.091	4.37 ± 0.08^c	0.03	7.85 ± 0.05	0.14	-1.75 ± 0.06	0.02
0.228	3.92 ± 0.07	0.12	7.44 ± 0.05	0.21	-2.20 ± 0.05	0.12
0.452	3.38 ± 0.10	0.14	6.46 ± 0.09	0.09	-2.94 ± 0.09	0.12
0.622	3.04 ± 0.14	0.19	5.63 ± 0.12	0.12	-3.50 ± 0.14	0.13

[a] mol L^{-1}.

[b] Complexes formation constants refer to equilibrium: $p\text{TMT}^+ + q\text{FA}^{3.5-} + r\text{H}_2\text{O} = (\text{TMT})_p(\text{FA})_q(\text{OH})_r{}^{(p-3.5q-r)} + r\,\text{H}^+$.

[c] Standard deviation.

Table 8. Calculated values of formation constants of TMT–alginate complex species in NaCl, at different ionic strengths and at $t = 25\,^\circ$C

I^a	$\log \beta_{110}{}^b$	$\lvert\Delta \log \beta_{\text{calcd-exp.}}\rvert$
0.105	2.87 ± 0.08^c	0.08
0.251	2.72 ± 0.06	0.16
0.499	2.72 ± 0.03	0.00
0.687	2.78 ± 0.05	0.01

[a] mol L^{-1}.

[b] Complex species formation refers to the equilibrium: $p\text{TMT}^+ + q\text{AA}^{4-} + r\text{H}_2\text{O} = (\text{TMT})_p(\text{AA})_q(\text{OH})_r{}^{(p-4q-r)} + r\,\text{H}^+$.

[c] Standard deviation.

formation percentage: about 60% maximum formation for TMT(FA)_2 and more than 80% for TMT(FA)(OH) species at pH = 5.8 and 8.5, respectively. In the same experimental conditions, TMT(AA) is the only complex species formed in the trimethyltin–alginate system with a high formation percentage (~50%) at pH ~7. At pH > 7.5 the simple hydrolytic species of trimethyltin, TMT(OH), predominates.

The diagrams were drawn for a TMT to L concentration ratio of $1 : 10^4$, presumably near to the real concentration ratio occurring in natural waters between toxic organometallic compounds and organic ligands.

Comparison with the stability of analogous systems

As pointed out in the Introduction, no quantitative data on the association of trimethyltin(IV) cation with the ligands here investigated are given in the literature and, therefore, no direct comparison can be made. Only few quantitative data are reported on the binding of triorganotin(IV) (TOT) association by soluble humic substance.[43,44] Arnold *et al.*[43] report results on the tributyltin and triphenyltin association with dissolved humic acids in NaClO_4 medium (10 and 100 mM) in order to evaluate the effect of pH and sodium concentration on the TOT partitioning between dissolved organic matter and water. The authors report $\log K = 4.6$ for the complex species TBT–L (TBT = tributyltin, L = generic dissolved organic matter as ligand) in 10 mM NaClO_4 medium. This value, obtained with a different technique, is in very good accordance with the $\log \beta_{110} = 4.34$ and 5.25 obtained in this work for the TMT–FA system at I (NaCl) = 0.091 and 0 mol L^{-1}, respectively. Since we hypothesize that interactions of TMT with fulvic acid mainly occur via carboxylic groups, it can be affirmed that also in the metal sequestration process, by generic dissolved natural organic matter in oxic conditions, the main binding sites, in the pH range of natural waters, are the carboxylic ones. To have a further confirmation to this hypothesis and to make comparison on the stability of the triorganotin–fulvate system, additional investigations were performed using the synthetic polyacrylate ligand (PAA

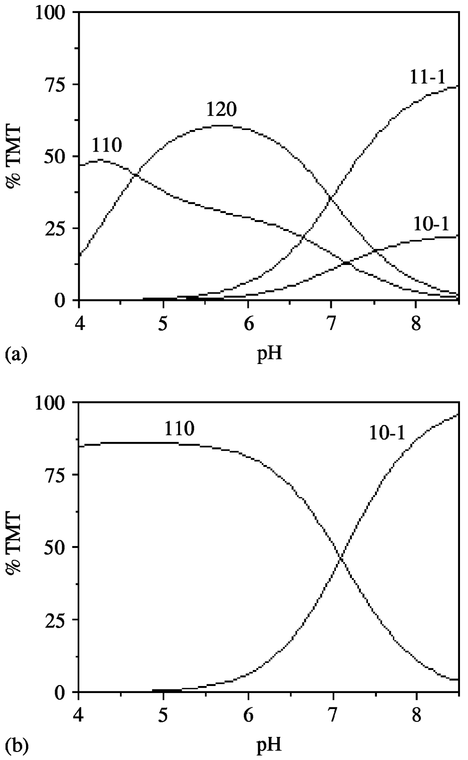

Figure 5. Speciation diagrams of trimethyltin(IV) vs pH in the TMT-FA (a) and TMT-AA (b) systems in NaCl ionic medium, at $I = 0.7$ mol L^{-1} and $t = 25\,^\circ$C. Indexes refer to $(\text{TMT})_p(\text{L})_q\text{H}_r{}^{(p-zq+r)}$ species. Experimental conditions: $C_{\text{TMT}} = 10^{-6}$ mol L^{-1}; $C_L = 10^{-2}$ mol L^{-1}.

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5.1 kDa), polyacrylic acid being a good model molecule of natural fulvic acid.[57] Acid–base properties of this ligand were previously investigated in our laboratories and its protonation and association constants in different ionic media and at different ionic strengths were reported in some recent papers.[56,58–60] Measurements were carried out on the TMT–PAA (5.1 kDa) system at $I = 0.5$ mol L^{-1}, in $NaNO_3$ ionic medium and at $t = 25\,°C$. Calculations gave evidence for a speciation model as that found in the TMT–FA system. Formation constants of the species are:

$$\log \beta_{TMT(PAA)} = 3.72 \pm 0.03$$

$$\log \beta_{TMT(PAA)2} = 5.70 \pm 0.02$$

$$\log \beta_{TMT(PAA)(OH)} = -2.67 \pm 0.04$$

The $\log \beta$ value obtained for the TMT(PAA) species (3.72 ± 0.02) obtained in $NaNO_3$ medium is comparable with the value of the corresponding species in the TMT–FA system (3.38 ± 0.10 in NaCl medium, see Table 7), confirming the similarity in the acid base behaviour of polyacrylate and fulvate ligands. Slight differences can be attributed to the influence of ionic medium. As in the case of TMT–FA system, a mixed hydrolytic species [TMT(PAA)(OH)] of comparable stability [$\log \beta = -2.67 \pm 0.04$ and -2.94 ± 0.09 for TMT(PAA)(OH) and TMT(FA)(OH) species in $NaNO_3$ and NaCl media, respectively] is also formed and it is the main species in the pH range (7–8) of interest of natural fluids, as shown in Fig. 6 [see for comparison Fig. 5(a)]. A partial contribution to the total complexation of TMT in both systems TMT–FA and TMT–PAA in the same pH range is also given by $TMT(L)_2$ species [Figs 5(a) and 6].

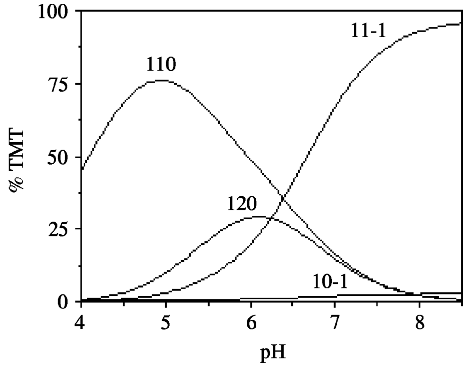

Figure 6. Speciation diagram of trimethyltin(IV) vs pH in the TMT–PAA (5.1 kDa) system at $I = 0.5$ mol L^{-1} in $NaNO_{3aq}$, and $t = 25\,°C$. Indexes refer to $(TMT)_p(L)_qH_r^{(p-zq+r)}$ species. Experimental conditions: $C_{TMT} = 10^{-6}$ mol L^{-1}; $C_{PAA} = 10^{-2}$ mol L^{-1}.

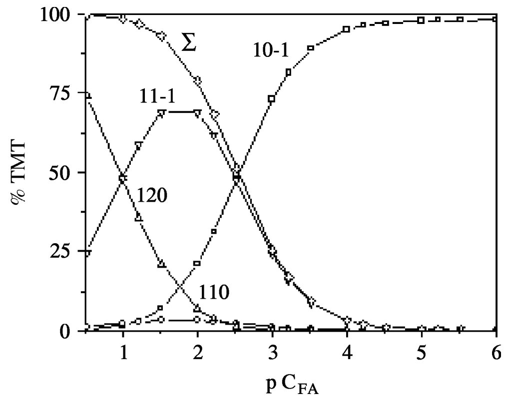

Figure 7. Speciation diagram of TMT vs $-\log C_L$ in the TMT-FA system, at pH = 8. Experimental conditions: I/NaCl = 0.7 mol L^{-1}; $t = 25\,°C$; $C_{TMT} = 10^{-6}$ mol L^{-1}. Indexes refer to $(TMT)_pL_qH_r^{(p-zq+r)}$ species. Σ refers to total percentage of TMT bound to ligand.

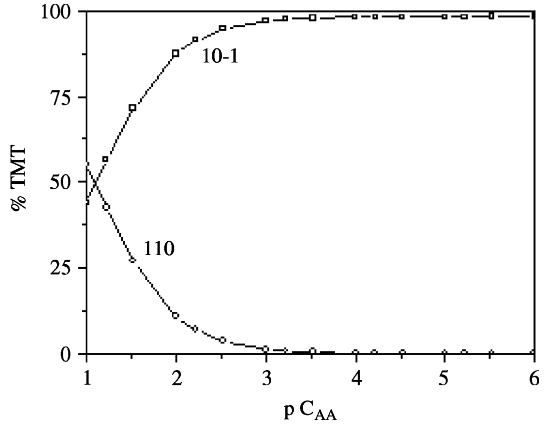

Figure 8. Speciation diagram of TMT vs $-\log C_L$ in the TMT-AA system, at pH = 8. Experimental conditions: I/NaCl = 0.7 mol L^{-1}; $t = 25\,°C$; $C_{TMT} = 10^{-6}$ mol L^{-1}. Indexes refer to $(TMT)_pL_qH_r^{(p-zq+r)}$ species.

Sequestering capacity of naturally occurring polycarboxylate ligands

The results obtained from speciation studies on the systems under investigation allow us to make some consideration about the lowest ligand concentration necessary to obtain a significant uptake of metal ions and organometallic compounds. This is an important problem, especially when the ligand is, as in this case, a chemical system really occurring in natural waters. The diagrams reported in Figs 7 and 8 can help us to find an answer to the above question. In these diagrams the formation percentages of trimethyltin(IV) species are plotted vs the logarithm of total ligand concentration (mol L^{-1}) for fulvic and alginic acid (Figs 7 and 8, respectively), and for a total concentration of trimethyltin cation $C_{TMT} = 10^{-6}$ mol L^{-1}, using experimental conditions (I/NaCl = 0.7 mol L^{-1} and pH = 8) very close to that of real seawater where NaCl is the main dissolved salt. As one can see, fulvic and alginic acids show, in these conditions, different coordination capability toward TMT cation. The sum

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of the complex species formed in the TMT–FA system (see curve Σ in Fig. 7) prevails over the formation percentage of the hydrolytic species of trimethyltin cation [10 – 1, TMT(OH)] to a concentration ratio of TMT : FA = 1 : 1000, at which about 50% of TMT is bound to the ligand.

In the same experimental conditions, alginic acid seems to be a worse sequestering agent than the fulvic acid: in fact, at pH = 8 (Fig. 8), a much greater ligand concentration (AA:TMT = 10^5) is needed to obtain the 50% of TMT sequestration.

In spite of that, since it has been found that alginic acid accounts for 10–40% of the dry weight of brown algae,[27] and also considering that triorganotin derivatives are generally present in seawater at very low concentrations, it is possible to suppose that such an alginate : triorganotin concentration ratio could be real in marine ecosystems.

The sequestration percentage of a metal ion by a ligand at different concentrations can be calculated using the following sigmoid-type Boltzman Equation:

$$P = P_\infty + \frac{P_0 - P_\infty}{1 + \exp[(pL - pL_{50})/S]} \tag{8}$$

where P is the total percentage of ML (in this case M = TMT; L = alginic or fulvic ligand) species calculated with respect to metal concentration; $pL = -\log[\mathrm{L}]_\mathrm{T}$; P_0 and P_∞ are the percentages for $pL \rightarrow 0$ and $pL \rightarrow \infty$, respectively; $pL_{50} = pL$ (for $P = 50\%$); S is an adjustable parameter which accounts for the slope in the flex of sigmoid curve. Since in our case $P_\infty = 0$ and $P_0 = 100$, Equation 8 becomes

$$P\% = \frac{100}{1 + \exp[(pL - pL_{50})/S]} \tag{8a}$$

where $P\%$ is the percentage of TMT–FA or TMT–AA complex species, and pL_{50} is the ligand concentration necessary to sequestrate 50% of the TMT. This equation allows calculation of the TMT sequestration percentage at every pH and ligand concentration values, after the formation constants for the systems under investigation and the species formation percentages vs pH have been defined. In Table 9 we report the parameters, calculated by equation 8, for the percentage sequestration of TMT (10^{-6} mol L^{-1}) by fulvate and alginate ligands in the pH range 6–8 of interest of natural waters, and at 0.7 mol L^{-1} ionic strength (NaCl ionic medium).

Table 9. Parameters of the equation (8) for a solution containing TMT$_\mathrm{tot}$ = 10^{-6} mol L^{-1} at I = 0.7 mol L^{-1}, in NaCl$_\mathrm{aq}$, at t = 25 °C and different pH values

	TMT–FA		TMT–AA	
pH	pL_{50}	S	pL_{50}	S
6	2.889	0.356	2.636	0.434
7	2.687	0.378	2.024	0.434
8	2.550	0.417	1.092	0.434

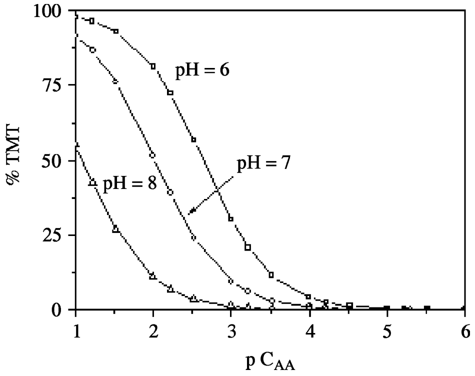

Figure 9. Percentage of trimethyltin(IV) as alginate complex species vs pC$_\mathrm{AA}$ at different pH values. Experimental conditions: t = 25 °C, I = 0.7 mol L^{-1} (NaCl$_\mathrm{aq}$), TMT$_\mathrm{tot}$ = 10^{-6} mol L^{-1}.

As can be seen, the sequestering capacity (pL_{50}) of alginic and fulvic ligands is higher at pH 6 and decreases with increasing pH. In fact, over pH 7, a consistent percentage of TMT simple hydrolytic species, of quite high stability, is formed. It is more evident for the TMT–AA system where no mixed hydrolytic species [TMT(L)(OH)], as in the TMT-FA system, is formed (see speciation model reported in Table 6).

In Fig. 9, the percentage of TMT (total concentration 10^{-6} mol L^{-1}) as alginate complex species is plotted vs alginate ligand concentration. As can be seen, at pH = 7, which is a value closer to that of fresh water, the sequestering ability of alginic acid towards TMT is 10 times more consistent than at pH = 8. In this case, in fact, a ligand concentration 10 times lower (AA : TMT ratio = 10^4) is necessary to have the same 50% sequestration of trimethyltin cation at the same concentration. That depends on the even more consistent formation of hydrolytic species of trimethyltin(IV) in the alkaline pH range. In fact, a more favourable TMT : AA ratio to obtain the same amount of TMT sequestration can be observed at pH = 6.

Analogously to TMT–FA and TMT–AA systems, we also calculated the sequestration capacity of PAA towards trimethyltin cation. By using the values of species formation constants determined at I = 0.5 mol L^{-1} (NaNO$_3$) reported above, calculations were performed at pH = 8 for a TMT concentration of 10^{-6} mol L^{-1}. Results are reported in Fig. 10.

By considering the formation of all TMT–PAA complex species, it can be observed that a ligand concentration of about $10^{-3.5}$ mol L^{-1} is necessary to obtain 50% sequestration of TMT (10^{-6} mol L^{-1}) by PAA, mainly as TMT(PAA)(OH) complex species (curve $\sum$, Fig. 10), being the remaining amount of TMT present as simple hydrolytic species [TMT(OH)]. To obtain 100% TMT uptake by PAA, at least 10^{-2} mol L^{-1} of sequestering agent is needed.

Comparison with sequestering capacity of low molecular weight polycarboxylate ligands

The sequestration capacity of polycarboxylate polyelectrolytes under investigation can also be compared with that of

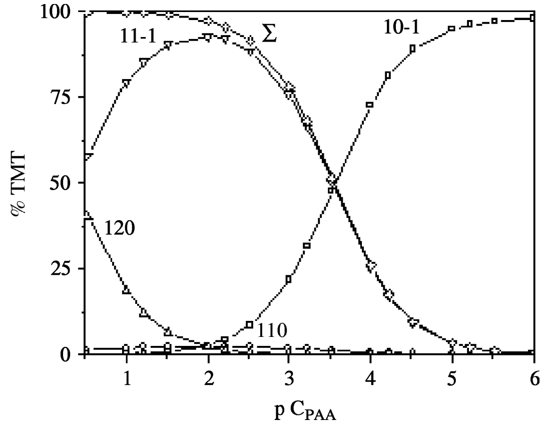

Figure 10. Speciation diagram of TMT vs $-\log C_L$ in the TMT–PAA system, at pH = 8. Experimental conditions: $I = 0.5$ mol L^{-1} in $NaNO_{3aq}$; $t = 25\,°C$; $C_{TMT} = 10^{-6}$ mol L^{-1}. Indexes refer to $(TMT)_pL_qH_r^{(p-zq+r)}$ species. Σ refers to total percentage of TMT bound to ligand.

Table 10. Sequestration capacity of low and high molecular weight polycarboxylate ligands (natural and synthetic) towards trimethyltin(IV) cation (10^{-6} mol L^{-1}) at different pH values, at $I = 0.5$ mol L^{-1}, in $NaCl_{aq}$ and at $t = 25\,°C$

	pH = 6		pH = 7		pH = 8	
Ligand	pL_{50}	S	pL_{50}	S	pL_{50}	S
tca	0.884	0.302	0.550	0.272	0.038	0.242
btc	0.814	0.227	0.610	0.194	0.222	0.188
mlt	2.205	0.434	1.708	0.435	0.791	0.434
AA	2.524	0.434	1.898	0.434	0.961	0.435
FA	3.352	0.363	3.237	0.394	3.164	0.425
PAA	3.465	0.423	3.554	0.431	3.548	0.433

other low molecular weight polycarboxylate ligands whose interactions with trimethyltin(IV) cation were previously investigated.[18] In particular, we consider the following tri-, tetra- and hexa-carboxylate ligands: propane-tricarboxylate (tricarballylate, tca), butane tetra-carboxylate (btc) and benzene hexa-carboxylate (mellitate, mlt). By using the pK values of all the species formed between trimethyl cation and the above cited carboxylate ligands,[18] the percentage formation of the species was calculated at fixed pH values and $I = 0.5$ mol L^{-1} (NaCl), and it was used to establish, by equation (8), the concentration of each ligand necessary to obtain 50% of trimethyltin sequestration. The results are reported in Table 10. In the same table, for a better comparison, the sequestration parameters of FA, AA and PAA ligands, in the same ionic strength conditions, are also reported.

As in the case of alginic and fulvic ligands, the sequestering capacity of low molecular weight carboxylic ligands towards triorganotin cation decreases with increasing pH, because TMT hydrolysis prevails (in the alkaline pH range) over the complex species formation. A different trend is shown by TMT–PAA system where the sequestering capacity of PAA is practically constant in the pH range 6–8, due to the formation, over pH 6, of a mixed species TMT(PAA)(OH) of fairly high stability.

In Fig. 11, the general picture of the sequestering capability of the different low and high molecular weight polycarboxylate ligands is reported at pH = 7 and 8 for a TMT concentration of 10^{-6} mol L^{-1}.

As expected, the sequestering capacity of low molecular weight ligands is less than that of polycarboxylate polyelectrolytes where the higher number of binding sites allows a higher stability to be obtained: moreover, as pointed out before, the sequestering capacity of fulvic and polyacrylic ligands is comparable due to the similar stability of complex species formed. The slightly higher binding ability of PAA must be attributed to a larger availability of carboxylate binding sites in the PAA linear structure rather than in the FA. The alginic ligand shows a smaller sequestration capacity than the PAA and FA, owing to a lower stability of species and, in general, to a minor number of complex species formed in the pH range investigated. In particular, since in the TMT–AA system only the TMT(AA) species is formed, the formation of

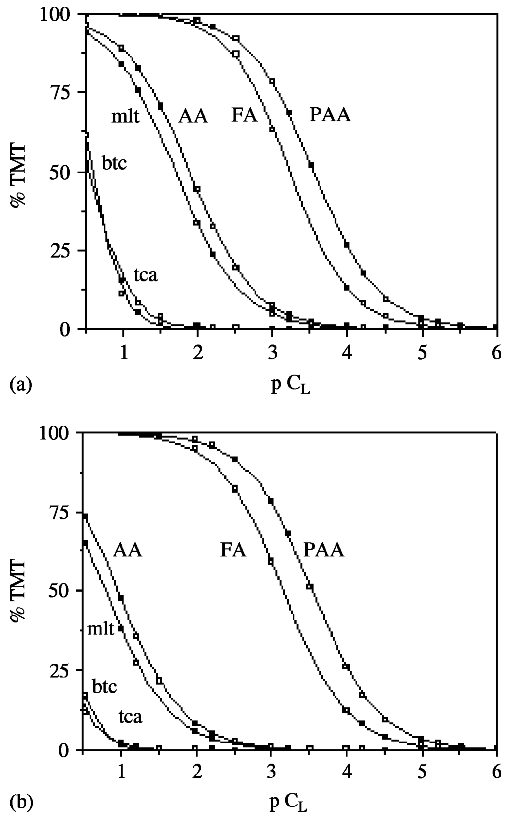

Figure 11. Sequestration percentage of trimethyltin(IV) by different ligands (L = tca, btc, mlt, PAA 5.1 kDa, FA and AA) vs pC_L. Experimental conditions: pH = 7 (a) and pH = 8 (b), $t = 25\,°C$, $I = 0.5$ mol L^{-1} $NaCl_{aq}$, $TMT_{tot} = 10^{-6}$ mol L^{-1}.

simple hydrolytic TMT(OH) species prevails over pH 7 with a consequent lowering of sequestering capacity of alginate ligand at pH 8 [Fig. 11(a) and (b)].

CONCLUSIONS

The sequestering capacity of naturally occurring organic polyelectrolytes toward metal ions and organometallic compounds can be established using the stability parameters of complex species formed and the species distribution in the pH range under investigation. Quantitative sequestration parameters of triorganotin cations by fulvic and alginic acids strongly depend on the number and type of complex species formed in both systems: the formation of a mixed hydrolytic species TMT(L)(OH) in the TMT–FA system allows the fulvic ligand to be a better sequestering agent than the alginic ligand also at pH > 7 where the TMT hydrolytic species formation is consistent.

The similarity of behaviour in the TMT–FA and TMT–PAA systems allow us to affirm that binding of metals and organometallic cations by natural organic matter in oxic conditions (i.e. in the absence of relevant concentration of thiol groups) mainly occurs via carboxylate groups in the pH range 5–8.

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