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Modelling of natural and synthetic polyelectrolyte interactions in natural waters by using SIT, Pitzer and Ion Pairing approaches

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Abstract

In this paper SIT and Pitzer models are used for the first time to describe the interactions of natural and synthetic polyelectrolytes in natural waters. Measurements were made potentiometrically at 25 °C in single electrolyte media, such as Et_4NI and NaCl (for fulvic acid $0.1 < I / mol\ L^{-1} < 0.75$), and in a multi-component medium simulating the composition of natural waters at a wide range of salinities (for fulvic and alginic acids: $5 < S < 45$) with particular reference to sea water [Synthetic Sea Water for Equilibrium studies, SSWE]. In order to simplify calculations, SSWE was considered to be a "*single salt*" BA, with cation B and anion A representing all the major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and anions (Cl^-, SO_4^{2-}) in natural sea water, respectively. The ion pair formation model was also applied to fulvate and alginate in artificial sea water by examining the interaction of polyanions with the single sea water cation. Results were compared with those obtained from previous speciation studies of synthetic polyelectrolytes (polyacrylic and polymethacrylic acids of different molecular weights). Results indicate that the SIT, Pitzer and Ion Pairing formation models used in studies of low molecular weight electrolytes may also be applied to polyelctrolytes with a few simple adjustments.
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1. Introduction

Natural waters can be considered multi-electrolyte solutions (Millero, 1974, 2002; Whitfield, 1975) and show a very large range of ionic strengths, from $I \sim 0.1$ mol kg^{-1} or less for freshwaters to $I \sim 0.7$ mol kg^{-1} or more for sea water, with some significant exceptions for hyper saline waters ($I > 6$ mol kg^{-1}). Therefore, in the construction of interaction models for natural waters, the dependence of the activity coefficients of components on ionic strength and ionic medium has to be allowed for. The most common models used for sea water speciation studies are: i) the ion pair formation model first proposed by Sillen (1961) and by Garrels and Thompson (1962), ii) the SIT (Specific ion Interaction Theory) model (Biedermann, 1975, 1986), and iii) the model proposed by Pitzer (Pitzer, 1973, 1991; Pitzer and Mayorga, 1973). Each of these models has its merits and shortcomings: ion pair formation models

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need a lot of stability data regarding the formation of weak complexes, whilst it is known that the determination of small stability constants is quite a difficult task in many cases; the classic SIT model gives good results only for some electrolyte solutions and ionic strength ranges (e.g. NaClO$_4$; $0.5 \leq I/\text{mol kg}^{-1} \leq 3.5$); the Pitzer model, in its complete formulation, is somewhat complicated and in evaluating calculation problems one must consider the co-linearity between different parameters and the risk of over-parameterization. On the other hand, ion pair formation models give an easily understandable picture of the network of interactions in a multi-component solution; SIT is quite simple to use; and Pitzer equations give a complete description of mixed electrolyte solutions, in particular when mixed parameters are taken into account. For both SIT and Pitzer models many parameters have been collected and reported for simple and mixed electrolytes (Ciavatta, 1980, 1990; Pitzer, 1991; Grenthe and Puigdomenech, 1997). Moreover, trace activity coefficients for a great number of species have been reported and hundreds of SIT and Pitzer parameters are reported every year in literature.

Most speciation studies in natural waters are mainly concerned with equilibrium analyses of the major components [with particular reference to the carbonate system in sea water (Millero, 1995, 2000)] and trace metals, especially as regards their hydrolytic processes and interaction with low molecular weight organic and inorganic ligands. The interaction of the proton and some metal ions of environmental interest with high molecular weight molecules has been extensively studied (see, for example, Tipping, 1998, 2002; Tipping et al., 1988, and reference reported therein) but the studies on the dependence of equilibrium constants on medium and on ionic strength are few, in particular as concern the application of models generally used for the interaction of low molecular weight ligands. Recently, some example of application of SIT to natural polyelectrolytes was reported (Rey-Castro et al., 2004; De Stefano et al., 2005).

With the aim of extending the use of SIT, Pitzer and ion-pair models to polyelectrolytes, it is proposed here for the first time (except for the Ion Pairing model) that the above models be applied in defining the chemical interactions of high molecular weight polycarboxylic ligands in aqueous solution. To this end, the acid-base behaviour of two typical naturally occurring polycarboxylates, fulvic acid (FA) and alginic acid (AA), was investigated in Et$_4$NI and NaCl single ionic media and in multi-component media simulating the composition of natural waters, with particular reference to sea water

[Synthetic Sea Water for Equilibrium studies, SSWE (De Stefano et al., 1994), i.e., Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$ and SO$_4^{2-}$ for fulvic acid, and Na$^+$, K$^+$, Mg^{2+}, Cl$^-$ and SO$_4^{2-}$ for alginic acid, respectively]. Results are compared to those obtained in previous speciation studies of synthetic polyacrylic and polymethacrylic acids (De Stefano et al., 2000a, 2002, 2003a,b, 2004). The protonation of these ligands was studied potentiometrically and dependence on dissociation degree was taken into account by the three parameter equation proposed by Högfeldt et al. (1989). Measurements in Et$_4$NI, NaCl and SSWE ionic media were performed at 25 °C in the ionic strength and salinity ranges 0.1–0.75 mol L^{-1} and 5–45 respectively. To reduce the complexity of the system under investigation and to simplify calculations, SSWE was considered to be a single salt (BA), with cation B and anion A representing all the cations and anions in synthetic sea water (De Stefano et al., 1998). The treatment of protonation and complex formation data using both SIT and Pitzer models gave encouraging results. Worth mentioning is the fact that these models allowed the simultaneous calculation of interaction parameters and mean polyanion charges as a function of dissociation degree. Some empirical relationships are also proposed.

2. Experimental

2.1. Reagents and materials

All reagents were of analytical grade. Fulvic acid was supplied by International Humic Standard Society (IHSS, lot n. 2S102F). Alginic acid extracted from *Macrocystis pyrifera* was from Sigma (lot n. 60K1443). Hydrochloric acid and sodium hydroxide solutions were standardised against sodium carbonate and potassium biphthalate, respectively. Sodium, calcium, potassium and magnesium chlorides and sodium sulphate, used to prepare synthetic sea water solutions, were always dried before use. Calcium and magnesium chlorides were standardised against EDTA. The concentration of sulphate solutions was checked by an ion chromatographic analyser (Dionex Sunyvale, CA, USA; model DX500) coupled with a conductometric detector. Details of the composition of synthetic sea water are reported in Table 1. All the solutions were prepared using CO$_2$-free freshly prepared distilled water ($R = 18\ M\Omega$).

2.2. Equipment and procedure

Measurements were carried out using potentiometric apparatus consisting of a Metrohm mod. 665 auto-