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Coordination Chemistry Reviews 252 (2008) 1093–1107

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Weak alkali and alkaline earth metal complexes of low molecular weight ligands in aqueous solution

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Received 4 June 2007; accepted 8 August 2007
Available online 11 August 2007

Contents

Abstract

This work is aimed at reviewing the chemical literature dealing with thermodynamic aspects of the weak complex formation (species with log K values less than about 3) between alkali and alkaline earth metal ions with low molecular weight inorganic and organic ligands in aqueous solution. The following ligands (up to hexavalent anions) were examined in detail: (i) hydroxide, chloride, sulfate, carbonate and phosphate as inorganic,

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doi:10.1016/j.ccr.2007.08.005

and (ii) carboxylates, amines, amino acids, complexones and nucleotides as organic ligands. The paper also identifies the main reasons responsible for the dispersion of the stability data on ion pairs in the literature. When possible, the trend of stability for the different metal ions interacting with the same ligand will be considered to find predictive interaction relationships. Since the stability of weak alkali and alkaline earth metal complexes are mainly due to electrostatic interaction, simple empirical relationships were obtained between log *K* and the charge of the anionic ligand. The interest for alkali and alkaline earth cations rises since they are used in study of basic science as components of the supporting electrolyte and are widely diffused in natural fluids. Some examples of application of this science were presented too, to show the role of weak complex formation in the modelling process of natural systems.

Keywords: Alkali metal complexes; Alkaline earth metal complexes; Weak complexes; Formation and stability in aqueous solution; Ion pairs

1. Introduction

Sodium, potassium, calcium and magnesium ions are the major cation contributors to the inorganic composition of natural waters and biological fluids. In spite of their key role in many environmental and biological processes, such as membranes transport or metal metabolism [1], in which also lithium and strontium ions are often involved, coordination chemistry of alkali metal ions was relatively little investigated, especially if compared to transition metals. The main interest was focused on the interaction of alkali and alkaline earth cations with biologically active molecules, such as amino acids, proteins, sugars, nucleotides etc, especially to emphasize their biochemical functions. Most of the papers dealing with this subject can be found in specialized biomedical or biochemical journals. Bioinorganic chemistry investigations on this topic were performed mainly to define the structure of the complexes resulting by these interactions [2]. Stability data on complexes of alkali and alkaline earth metal ions in aqueous solution were reported by Midgley [3] and Poonia and Bajaj [4], with particular attention to complex formation with poly-aminocarboxylic and macromolecular ligands such as crown, cryptands and high molecular weight antibiotics. The interactions of alkali and alkaline earth metal ions with low molecular weight ligands were established many years ago [5] as ion pairs or weak complexes formation, but they have excited in general scarce interest for the following reasons: (i) formation constants are small and difficult to determine with high precision and accuracy; (ii) ion pair formation often occurs between the components of the supporting electrolyte and the cation and/or anion of the acid-base system under investigation; (iii) to separate unambiguously the effects of the medium from those of the short-range specific interactions in the formation of more stable complex species, a non-interacting medium is needed for each acid-base system under investigation (a reference baseline). This last point is not easy to obtain and, for this reason, many researchers prefer to use stoichiometric stability constants, i.e. strictly valid only in a specific medium.

The aforementioned reasons led to a certain dispersion of the stability data on weak complexes in the literature [6–18], mainly depending on some discriminating factors as: (i) results obtained by unreliable methods, (ii) lack of attention for those quantities significantly affecting the stability and/or the precision and accuracy of measurements, (iii) lack of equilibrium during measurements (for systems with complex kinetic), (iv) use of different thermodynamic scales as activity/concentration (sometimes mixed) or molar/molal, (v) incomplete evaluation of the uncertainty budget (weighted combination of all uncertainties on experimental quantities). The aim of this review is to give a picture of the stability data of ion pairs or weak complexes (with log *K* values less than about 3) formed by alkali or alkaline earth metal ions with low molecular weight inorganic and organic ligands. When possible, the trend of stability for the different metal ions interacting with the same ligand will be considered in order to find predictive interaction relationships. To this end, the following ligands will be examined in detail: hydroxide, chloride, sulfate and phosphate as inorganic and carboxylates, amines, amino acids, complexones and nucleotides as organic ligands. The interaction with other inorganic and organic ligands, such as fluoride, hexacyanoferrate(III) and hexacyanoferrate(II), phenols and some nucleotides will be also considered. Finally, few applications showing the need of taking into account the formation of weak complexes to describe in a rigorous way the aqueous natural and biological systems will be examined.

When the values of formation constants were determined at different ionic strengths, the best comparison among them can be made by an extrapolation to infinite dilution, even if different approaches were employed for extrapolation, and the resulting values often are very close to each other. So we preferentially report values at zero ionic strength. If the authors did not propose their thermodynamic value, we have calculated it by an extended Debye–Hückel type equation [19]. The values here reported are at $t = 25\,^{\circ}\mathrm{C}$ (different temperatures are pointed out).

2. The determination of small formation constants

2.1. Experimental methods and techniques

All the classic experimental methods and techniques were used for the determination of the formation constants and thermodynamic parameters (ΔG and ΔH) of weak complexes. A review of these methods together with the physico-chemical approaches in defining ion pairs was reported recently by Marcus and Hefter [20]. Among experimental techniques, the potentiometric one, using glass electrodes and ISE-M (M = different metal ions), was adopted in many laboratories, for its characteristics of simplicity and economicity. Potentiometry coupled with Harned cell was also used for the quantitative determination of OH^--alkali and alkaline earth interaction [21,22].

The formation of alkali metal complexes with Nitrilotris (methylenephosphonates) [23] was studied by dilatometry, ^{31}P NMR and potentiometry, both in aqueous solution and at solid state. NMR was used to investigate hydrolysis equilibria of alkali metal ions [24]: the extent of the chemical shift (^{7}Li, ^{23}Na, ^{39}K and ^{133}Cs NMR), sensitive to both pH and ionic strength, is used to estimate the hydrolysis constants for the above alkali metal ions. ^{13}C NMR is also used for ion pairs formed between organic ligands, such as carboxylic acids, and alkaline earth metal ions [25]. NMR technique was also coupled to potentiometry in investigating alkali metal complexes with citrate [26]. Calorimetry coupled with ISE-H$^+$ potentiometry was employed [27,28] to investigate Na$^+$ or K$^+$ ion pairs formation with citrate, tartrate or malate ions, while Na$^+$ or K$^+$-sulfate ion pairs were also studied by calorimetric technique [29,30]. By means of the ultraviolet circular dichroism (CD) spectroscopy, data were obtained (at different ionic strengths) on the ion pairs formation between alkali metal ions and chiral carboxylic acids of biochemical interest [31,32], through the recording of spectropolarimetric signal variations in the range 210–215 nm (carbonyl chromophore). Mass spectrometry is also used [33–35] to achieve structural indications, out of strict equilibrium conditions, of species obtained in solution. Theoretical approach for bond energies calculations related to IR [36] or mass [35] spectra are also considered.

The adoption of particular methods is necessary when dealing with these complexes. For example, from acidimetric measurements information about the proton displacement reaction M + HL = ML + H (charges omitted) can be obtained, but if $K < 100$ the difference between the concentration of proton bound to L and the free proton concentration is to low to allow reliable calculations. Therefore, generally the self-medium method is preferred in order to enhance the above difference. Often, the comparison between protonation constants obtained in a medium considered not interacting and in a supporting electrolyte whose cation forms weak complexes, $\Delta\log K^{\mathrm{H}}$, gives information on the strength of the interaction, through the simple equation [37]:

$$\log K_{\mathrm{M}} = \frac{(10^{\Delta \log K^{\mathrm{H}}} - 1)}{C_{\mathrm{M}}} \tag{1}$$

where K_{M} is the formation constant of the weak complexes. This method, often called $\Delta\log K^{\mathrm{H}}$ or ΔpK method, implies the assumption γ(baseline electrolyte) = γ(interacting electrolyte), that holds only under some conditions.

The main problem in the determination of small formation constants concerns the possibility of separating medium and interaction effects. This is a particularly crucial problem at high ionic strengths, when the activity coefficients of different electrolytes may vary considerably [38]. In many cases, it was assumed that by substituting the supporting electrolyte (not interacting) by at last 10% of an electrolyte containing the interacting cation, activity coefficients do not vary significantly also at high ionic strengths, namely $I \geq 3\,\mathrm{mol\,L^{-1}}$.

The determination of enthalpy and entropy changes can be carried out by calorimetric titration or by formation constant determination at different temperatures. Both methods, when dealing with very weak species, give ΔH values affected by large errors.

2.2. *Calculations*

General computer programs are available to calculate stability constants from potentiometric, spectrophotometric, NMR and calorimetric data [39]. Protonation constants in different electrolytes are used by some computer programs to calculate weak complexes between ligand and cation or anion of supporting electrolyte [40,41]. The dependence on ionic strength may be considered together with the determination of K, as given in some computer programs [40,41]. Calculations are performed, almost exclusively, by the least squares method, using the Marquardt algorithm.

2.3. *Activity coefficients and dependence on ionic strength of formation constants*

For a simple species ML the formation constant is given by:

$$K = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} = \frac{a_{\mathrm{ML}}/\gamma_{\mathrm{ML}}}{(a_{\mathrm{M}}/\gamma_{\mathrm{M}})(a_{\mathrm{L}}/\gamma_{\mathrm{L}})} = K^0\frac{\gamma_{\mathrm{M}}\gamma_{\mathrm{L}}}{\gamma_{\mathrm{ML}}} \tag{2}$$

The activity coefficient can be expressed as:

$$-\log\gamma = z^2\mathrm{DH} + F(I, p) \tag{3}$$

where DH is the Debye–Hückel term, and F(I, p) is a function of I and some parameters p. In Eq. (2), K^{o} represent the formation constant at infinite dilution. Different types of Eq. (3) were proposed [42–45], two of which are the most popular in investigations relative to protonation, hydrolysis and complex formation equilibria. The first one is the so-called SIT equation (from the acronym Specific ion Interaction Theory) based on the principle of specific interaction of ions, introduced by Brönsted [46] and implemented by Scatchard [47] and Guggenheim and Turgeon [48]. According to SIT:

$$\mathrm{DH} = \frac{A_\gamma\, I^{1/2}}{(1 + 1.5\, I^{1/2})} \tag{4}$$

and

$$F(I, p) = \Sigma\varepsilon_i m_i \tag{5}$$

where ε_i are the specific ion interaction coefficients, and m_i are the molal concentrations. A more sophisticated approach is given by the Pitzer [42] equations, where:

$$\mathrm{DH} = A_\phi[I^{1/2}(1 + 1.2\, I^{1/2})^{-1} + 1.667\,\ln(1 + 1.2\, I^{1/2})] \tag{6}$$

and

$$F(I, p) = f(\beta^{(0)}, \beta^{(1)}, \beta^{(2)}, C^{(\phi)}, \theta, \psi) \tag{7}$$

where $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $C^{(\phi)}$ are interaction parameters between two ions of opposite sign, θ is an interaction parameter between two ions of the same sign (+ +, − − interactions), ψ is a triplet interaction parameter (+ − +, − + −). Considering Eq. (2), the formation constant can be written

$$\log K = \log K^0 + \Delta z^2\mathrm{DH} + \Sigma F(I, p) \tag{8}$$

where $\Delta z^2 = \sum(\mathrm{charges})^2_{\mathrm{products}} - \sum(\mathrm{charges})^2_{\mathrm{reactants}}$ (in many works the parameter $z^* = -\Delta z^2$ was used [19,40]).

Note that by using both SIT and Pitzer approaches, formation constants and ionic strength have to be expressed in the molal concentration scale, mol kg^{-1}.

The numerical values and the trends of parameters p (Eq. (3)), can be used to evaluate the stability constants of weak complexes. By comparing the activity coefficients, $\gamma_{\pm}$, of alkali metal hydroxides and chlorides, Baes and Mesmer [21] calculated the equilibrium constants relative to the formation of LiOH, NaOH and KOH very weak species. By considering the parameters of Pitzer equations it is possible to calculate the formation constants of weak complexes from the interaction coefficient $\beta^{(2)}$ [49], using the approximation $\log K = \log(-2\ \beta^{(2)})$.

The dependence of ΔH on ionic strength can be modelled by using SIT equation in the form:

$$\Delta H = \Delta H^0 + \frac{1.5\Delta z^2\ I^{0.5}}{1 + 1.5I^{0.5}} + +\Delta\varepsilon' I \qquad (9)$$

with $\Delta\varepsilon' = RT^2\ \ln 10\ \partial\Delta\varepsilon/\partial T$.

3. Inorganic ligands

3.1. Hydrolysis

Although the alkali metal hydroxides are generally considered as completely dissociated, there is evidence to suggest that weak MOH species are formed, in particular with regard to Li^+. The strongest evidence comes from the trend of activity coefficients of alkali metal chlorides, bromides and iodides, $Li^+ > Na^+ > K^+ > Cs^+$, which is the opposite for alkali metal hydroxides, $Li^+ < Na^+ < K^+ < Cs^+$. These sharply different trends suggest association between M^+ and OH^- [50]. From the extensive measurements of Harned and his co-workers [51–55] (K_w determination in different supporting electrolytes in a wide range of ionic strengths), Baes and Mesmer [21] obtained reliable estimates of formation constants for MOH ion pairs, assuming no interaction between Cs^+ and OH^- ($\log K = 0.36$, -0.18 and -0.46 for Li^+, Na^+ and K^+ respectively, at 25 °C). Gimblet and Monk [22], using the Harned cell, determined quantitatively the interaction of OH^- with Li^+ and Na^+ at different temperatures ($\log K = 0.18$ and -0.68 for Li^+ and Na^+, respectively, at 25 °C). Some experiments in this field were also performed by conductimetry, but only qualitative evidence was obtained [56,57]. Using the comparative method [see Eq. (1), with $\Delta pK_w = pK_w\ (Et_4NI) - pK_w\ (MCl)$], formation constants were obtained at different ionic strengths ($\log K = 0.53$, 0.28 and 0.18 for Li^+, Na^+ and K^+ respectively, at 37 °C [58]). A careful study was performed by Ohtaki [59] in 3 mol L^{-1} $NaClO_4$: the LiOH formation constant obtained potentiometrically (glass electrode) is $\log K = -0.18$. This low value, in comparison with other reported values, is clearly due to the simultaneous hydrolysis of Na^+, not taken into account in the calculation. A comparative NMR study (^7Li, ^{23}Na, ^{39}K and ^{133}Cs) [24] gave evidence for the formation of MOH^0 species for all these alkali metals ($\log K = -0.10$, -1.0, -0.8 and -0.8, for Li^+, Na^+, K^+ and Cs^+, respectively, at $I = 3.4$ mol L^{-1} Me_4NCl/Me_4NOH and 25 °C).

Magnesium cation undergoes hydrolysis at low concentration giving the species $MgOH^+$ with $\log K \sim 2.6$ [21]. Palmer and Wesolowski [60] performed a careful study on the first hydrolysis quotient of Mg^{2+} from 0 to 250 °C giving reliable values of formation constants for the equilibrium $Mg^{2+} + H_2O = Mg(OH)^+ + H^+$ ($^*K$). At higher concentrations ($C_{Mg} > 0.5$ mol L^{-1}), the species $Mg_4(OH)_4{}^{4+}$ is formed, as clearly demonstrated by Lewis [61] and Baes and Mesmer [21]. In the range $1 \le C_{Mg} \le 1.5$ mol L^{-1}, Lewis obtained $\log{}^*\beta\ [Mg_4(OH)_4] = -39.82$ to -39.76. The hydrolysis extent of calcium, strontium and barium cation is much lesser with respect to that exhibited by magnesium, and Baes and Mesmer [21] report $\log K$ values ranging from 1.2 to 0.5 as we proceed from Ca^{2+} to Ba^{2+}. These figures were obtained by comparing the activity coefficients of alkaline earth metal with alkali metal chlorides [37]. Other formation constants, using the Harned cell, were reported by Gimblet and Monk [22] at different temperatures. Using the ΔpK_w (Eq. (1)) method, calcium association with OH^- was also studied at different temperatures [37] giving $\log K = 1.30 + 0.0071\ (t - 25)$. From the dependence on temperature of association constants, ΔH^0 values were also obtained ($\Delta H^0 = 1.3$ and 2.1 kJ mol^{-1}, for Na^+ and Ca^{2+}, respectively [37]).

There is no doubt that alkali metal cations undergo hydrolysis but the extent of $M(OH)^0$ in solution is too small to be estimated with acceptable errors. Only for Li^+, a tentative value (at $I = 0$ mol L^{-1}, $t = 25$ °C) can be given: $\log K = 0.4 \pm 0.2$. For Ca^{2+} a good estimate, in the same conditions, is $\log K = 1.30 \pm 0.05$. For $Mg(OH)^+$, the values of $\log K$, ΔH and ΔS reported by Palmer and Wesolowski [60], in a wide range of ionic strength and temperature, are to be recommended. The equilibrium constant for $Mg_4(OH)_4{}^{4+}$ must still be checked.

3.2. Chlorides

Chloride complexes of alkali metal cations are very weak and were studied by partial molal volume and potentiometric measurements [62,63]. In particular, Millero obtained $\log K = -0.46$, -0.74 and -0.96 for sodium complex species NaCl at 0, 25 and 55 °C respectively, in the ionic strength range 0.25–1 mol L^{-1}. Johnson and Pytkowicz reported $\log K = -0.49$ and -0.33 for NaCl and KCl, respectively, at $I = 0.6$ mol L^{-1} and 25 °C. From the dependence on temperature, a value of $\Delta H^0 = -5$ kJ mol^{-1} for the sodium chloride ion pair is obtained (data from Millero).

Calcium and magnesium cation-chloride ion pairs are five to six times stronger than those of alkali metal cations, as reported in several studies. Among others, Johnson and Pytkowicz [63] report $\log K = 0.28$ and 0.35 for $CaCl^+$ and $MgCl^+$, respectively, at $I = 0.6$ mol L^{-1} and $t = 25$ °C. By ISE-Cl^- measurements [64], $\log K = 0.42$ and 0.49 for $CaCl^+$ and $MgCl^+$, respectively, were obtained at $I = 0$ mol L^{-1} and $t = 25$ °C.

De Robertis et al. [65], by a careful analysis of literature data, calculated the formation constant (and ΔH^0 values) of NaCl, KCl, $MgCl^+$ and $CaCl^+$ ion pairs, at different temperatures and ionic strengths. At $I = 0$ mol L^{-1} and $t = 25$ °C, they proposed for NaCl: $\log K = -0.30$, $\Delta H^0 = -8$ kJ mol^{-1}; for KCl:

$\log K = -0.27$, $\Delta H^0 = -4\,\mathrm{kJ\,mol^{-1}}$; for $MgCl^+$: $\log K = 0.57$, $\Delta H^0 = 5\,\mathrm{kJ\,mol^{-1}}$; for $CaCl^+$: $\log K = 0.40$, $\Delta H^0 = 7\,\mathrm{kJ\,mol^{-1}}$.

Other evidence for the formation of weak ion pairs of alkali metal chlorides was reported based on non-empirical quantum chemical methods [66] and molecular dynamics [67]. In particular two kinds of association models for Na^+-Cl^- were observed, namely, contact ion pairs and solvent separated ion pairs. Heyrovská [68] showed that the non-ideal thermodynamic properties of strong electrolytes are due to partial dissociation.

3.3. *Sulfates*

Owing to the relevance of sulfate in many natural fluids, its complexes with alkali and alkaline earth metal ions were investigated by several authors [29,69–78] some of which reported also ΔH^0 values. The stability of sulfate ion pairs with alkali and alkaline earth metal ions is slightly higher than that of the corresponding chloride species. Formation constants of Li^+, Na^+, K^+, Rb^+ and Cs^+ sulfate complexes were determined at 37 °C and in the ionic strength range $0.03 < I < 0.5\,\mathrm{mol\,L^{-1}}$ for biological application purposes [75]. The values of $\log K = 0.79$ (Li^+), 0.39 (Na^+), 0.52 (K^+), 0.60 (Rb^+) and 0.69 (Cs^+) were reported. The trend of the stability constants exhibits a sharp minimum (sodium) which is absent or less evident with other ligands while for alkaline earth metal ions the constant values show an increasing trend ($\log K = 2.5$ for Sr^{2+} and 2.72 for Ba^{2+} [79]). As it happens for the other ligands, the formation constants for alkaline earth metal ion complexes are more than one order of magnitude higher with respect to the species of alkali metals. Evidence for sodium, calcium and magnesium ion pairs formation is given also by Raman spectroscopy [80].

3.4. *Carbonates*

Many investigations were reported in the literature on aqueous carbonate solutions due their importance in natural systems. Most of papers concern protonation constants while little is known about the interaction with alkali metal cations. For the $NaCO_3^-$ species Garrels and Thomson [81] reported $\log K = 1.27$ ($I = 0\,\mathrm{mol\,L^{-1}}$, $t = 25\,°C$), while data at different ionic strengths are reported by Butler and Huston [82] ranging from 0.96 at $I = 0$ to 0.43 at $3\,\mathrm{mol\,L^{-1}}$ (NaCl). Pytkowicz and Hawley [83] determined in seawater (34.8‰ salinity) $\log K = 0.63$. Potentiometric investigation of weak $NaCO_3^-$ association was reported by Capewell et al. [84], Roy et al. [85] and Mojica-Prieto and Millero [86]. Recently, Crea et al. [87] calculated formation constants for sodium carbonate and hydrogencarbonate species from differences between protonation constants in Et_4NI, considered as baseline, and protonation constants in NaCl and proposed $\log K = 1.15$, 0.26 and −0.25 for $NaCO_3^-$, $Na(HCO_3)^0$ and Na_2CO_3 (reaction: $Na^+ + NaCO_3^-$) species, respectively.

Complexes of carbonate with alkali earth metal cations are not weak and for this reason they are not considered in this paper. The hydrogencarbonate anion interacts weakly with alkaline earth metal cations. Most of data were collected by Palmer and Eldik [88]: for the $Mg(HCO_3)^+$ and $Ca(HCO_3)^+$ species mean formation constant values are $\log K = 1.08$ and 1.03, respectively.

3.5. *Phosphates*

Aqueous solution chemistry of phosphate in its inorganic and organic forms was largely investigated. Stability data on the complex species formation of inorganic phosphate with alkali and alkaline earth metal ions have reported by different authors [58,89–95]. The stability of dihydrogenphosphate$^-$ with Na^+ and K^+ is nearly the same ($\log K = 0.28$ and 0.26, respectively, for the reaction $M^+ + H_2PO_4^- = M(H_2PO_4)$ [92]). A comparison can be made with carboxylate complexes: with respect to the range that can be derived for formation constants of sodium species with monocharged carboxylate ligands (−0.31 to 0.42) these values approach to the upper limit. The stability of the alkali metal species with hydrogenphosphate^{2-} (for reaction $M^+ + HPO_4^{2-} = M(HPO_4)^-$, $\log K = 1.08$, 1.02 and 0.87 for Li^+, Na^+ and K^+, respectively [89,92]) shows the trend expected according to the charge/radius ratio. Analogous trend is shown by phosphate^{3-} complexes: $\log K = 1.60$ ($t = 37\,°C$, [58]), 1.43, 1.37 for Li^+, Na^+ and K^+, respectively [92]. With regard to the alkaline earth cations, the species of magnesium are somewhat more stable than those of calcium, with a general stability trend $Mg^{2+} > Ca^{2+} > Sr^{2+}$: for the reaction $M^{2+} + H_2PO_4^- = M(H_2PO_4)^+$, $\log K = 1.60$ and 1.41 for Mg^{2+} and Ca^{2+}, respectively [91,94,95]; for the reaction $M^{2+} + HPO_4^{2-} = M(HPO_4)$, $\log K = 2.85$, 2.64 and 2.27 for Mg^{2+}, Ca^{2+} and Sr^{2+}, respectively [90,91,93–96]. As expected, all these values are significantly higher than the ones determined for the corresponding alkali metal complexes.

Diphosphate ($H_4P_2O_7$) and triphosphate ($H_5P_3O_{10}$) form more stable alkali metal complexes than the corresponding ones of phosphate, with the same trend of stability [97–100]. Log K values for diphosphate and triphosphate complexes with lithium, sodium and potassium are reported in Table 1. In the same table we report the stability data given by De Stefano et al. [95] on the formation of homo and hetero (Na/K) binuclear species in different alkali metal phosphate systems. For all these species the trend of stability is strictly dependent on the charge of the ligand.

3.6. *Other ligands*

As concerns fluoride ligand, stability data in aqueous solution were collected by Bond and Hefter [101]. They reported as doubtful data $\log K = -0.56$ ($I = 1\,\mathrm{mol\,L^{-1}}$, $t = 25\,°C$) for NaF species. Miller and Kester [102] determined the stability of sodium fluoride ion pairs in seawater medium. Stability constants of MgF^+ ($\log K = 1.36$) and CaF^+ ($\log K = 0.89$) determined by using a fluoride ion selective electrode ($I = 0.7\,\mathrm{mol\,L^{-1}}$, $NaClO_4$) were reported by Elgquist [103].

Alkali metal complexes of hexacyanoferrate(II) were studied in different laboratories [104–106] using different techniques, and show always the stability trend $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. The whole accordance among different reported values is fairly good. Mean values for $\log K$ [ML] are (±0.1): 2.0 (Li^+), 2.3

Table 1
Values of log K ($I = 0\ \mathrm{mol\ L^{-1}}$, $t = 25\ ^\circ\mathrm{C}$) for mono-, di- and triphosphate-alkali metal systems

Reaction	Li^+	Na^+	K^+	Na/K	Refs.
$M^+ + MPO_4{}^{2-} = M(MPO_4)^-$		1.2	0.8		[95]
$M^+ + MHPO_4{}^- = M(MHPO_4)$		0.23	−0.08		[95]
$M^+ + M^{+\prime} + PO_4{}^{3-} = MM'(PO_4)^-$				2.8	[95]
$M^+ + M^{+\prime} + HPO_4{}^{2-} = MM'(HPO_4)$				1.3	[95]
$M^+ + P_2O_7{}^{4-} = MP_2O_7{}^{3-}$	3.71	2.25	2.24		[97–99]
$M^+ + HP_2O_7{}^{3-} = M(HP_2O_7)^{2-}$	2.00	1.65	1.52		[97–99]
$M^+ + MP_2O_7{}^{-3} = M(MP_2O_7)^{2-}$		1.7	1.0		[95]
$M^+ + MHP_2O_7{}^{2-} = M(MHP_2O_7)^-$		0.2	0.2		[95]
$M^+ + M^{+\prime} + P_2O_7{}^{4-} = MM'(P_2O_7)^{2-}$				4.1	[95]
$M^+ + M^{+\prime} + HP_2O_7{}^{3-} = MM'(HP_2O_7)^-$				2.1	[95]
$M^+ + P_3O_{10}{}^{5-} = MP_3O_{10}{}^{4-}$	3.47	2.33	2.33		[98–100]
$M^+ + HP_3O_{10}{}^{4-} = M(HP_3O_{10})^{3-}$	2.34	2.18	2.10		[98–100]
$M^+ + MP_3O_{10}{}^{4-} = M(MP_3O_{10})^{3-}$		2.7	1.8		[98–100]
$M^+ + MHP_3O_{10}{}^{3-} = M(MHP_3O_{10})^{2-}$		0.8	0.4		[98–100]
$M^+ + MH_2P_3O_{10}{}^{2-} = M(MH_2P_3O_{10})^-$		0.1	−0.3		[98–100]
$M^+ + M^{+\prime} + P_3O_{10}{}^{5-} = MM'(P_3O_{10})^{3-}$				5.1	[95]
$M^+ + M^{+\prime} + HP_3O_{10}{}^{4-} = MM'(HP_3O_{10})^{2-}$				3.0	[95]

(Na^+), 2.5 (K^+), 2.7 (Rb^+) and 2.9 (Cs^+). The formation of M_2L species was also proposed with a stability proportional to that of 1:1 complexes according to the relationship log β [M_2L] = 0.18 + 1.27 log K [ML]. From the dependence on temperature approximated ΔH^0 and ΔS^0 were obtained, with a mean values for Li^+, Na^+ and K^+ complexes $\Delta S^0 = 120 \pm 40\ \mathrm{kJ\ mol^{-1}}$. An extensive study [105] in Li^+/Na^+, Li^+/K^+, Na^+/K^+ mixed chloride solutions gave evidence for the formation of MM′L species. The constant for the equilibrium $M_2L + M_2'L = 2\,MM'L$ showed a mean value log $X = 1.1 \pm 0.2$ for all the mixed systems, indicating a significant stabilization for the mixed complexes (the statistical value is log $X = 0.6$ [107]).

Hexacyanoferrate(III)-alkali metal complexes are significantly less stable (about one log unit) and follow the same trend of hexacyanoferrate(II) species [108,109]. Data on pentacyanide cobalt(II) are reported only for Rb^+ complex, with the average value log $K = 0.57$ [110].

A particular class of ligands that forms quite stable alkali metal complexes is represented by *myo*-inositol-n-phosphates ($n = 1\ldots6$). *Myo* inositol hexa phosphate (structure is shown in another review of this volume), also known as phytate, forms several $M_iH_rL^{-(12\text{-}i\text{-}r)}$ species ($M = Li^+$, Na^+, K^+) [111–114] showing stability fairly high. For example, log K for reaction $M^+ + H_5L^{7-} = M(H_5L)^{6-}$ are 3.9 (Li^+), 3.5 (Na^+), and 3.4 (K^+), and log K for reaction $M^+ + H_6L^{6-} = M(H_6L)^{5-}$ are 2.8 (Li^+), 2.4 (Na^+) and 2.2 (K^+) [112,114]. *Myo*-inositol-triphosphate forms complexes with alkali metal cations [115] having very similar stability; an average value of log K ($M^+ + L^{5-} = ML^{4-}$) is 3.4 (from Li^+ to Cs^+).

4. Organic ligands

4.1. Carboxylates

Carboxylates are the most common and ubiquitous naturally occurring organic complexants, present in all the fractions of natural organic matter. Their characteristics of *hard* ligands lead to the formation of ion pairs with alkali and alkaline earth metal ions whose stability was widely investigated.

If compared with other basic non-charged groups (such as nitrogen containing donors or hydroxyl groups), carboxylate ligands with their ionic character are favoured in the formation of complexes with alkali metal ions. The values of formation constants of these species are strongly dependent on the number of carboxylate groups in the ligand molecule. In fact the value of log K for NaL species regularly increases with raising the number of charged carboxylate groups, from acetate to benzenehexacarboxylate.

Literature data reported in Table 2 illustrate the large number of carboxylate-alkali and alkaline earth metal complexes till now investigated. The whole of the data strongly confirms that the number of charges involved in the complex formation reaction is the most effective factor and suggests that the species in solution are mainly formed through ionic interactions. In particular, the log K values for NaL species of 16 dicharged dicarboxylate ligands, range from 0.65 to 1.18, while for the same sodium complexes with seven tricharged carboxylate ligands the values of log K range from 1.25 to 1.54. Although the difficulty in the determination (and, as a consequence, the uncertainty) of formation constants is greater for species involving alkali metals and monocharged carboxylate ligands, their values of log K for NaL type species range from −0.31 to 0.42: these values confirm the above suggestions with regard to the importance of the ligand charges.

For the most part of the ligands reviewed, the alkali metals studied are lithium, sodium and potassium. The decrease observed in formation constant values with increasing atomic number (for Li^+, Na^+ and K^+), very often related to the lowering of charge/radius ratio, is not always confirmed, when data for Rb^+ and Cs^+ are available as well: log K values with Rb^+ and Cs^+, respectively, are for acetate −0.16 and −0.12 [116]; for malate 0.47 and 0.23 [117,118]; for hydrogencitrate 0.95 and 0.92 [119]; for citrate 1.04 and 1.58 for Rb^+ [118,119], and 0.88 and 1.58 for Cs^+ [118,119].

Table 2
Values of log K for 1:1 carboxylate-alkali and alkaline earth metal complexes, at $t = 25\,^{\circ}\mathrm{C}$ and $I = 0\ \mathrm{mol\,L^{-1}}$

L	Li^{+}	Na^{+}	K^{+}	Ca^{2+}	Mg^{2+}	Refs.
Acetate^{-}	0.04	−0.11	−0.27	0.93	0.94	[19,116,120,205,209]
	0.29	−0.18		0.92	1.28	
	0.26	−0.07		1.12	0.88	
				0.90		
Salicylate^{-}		−0.31	−0.31	0.72		[19]
Propionate^{-}				0.87	0.91	[120]
Butyrrate^{-}				0.88	0.90	[120]
Hydrogenmalonate^{-}		−0.04		0.89		[19,120]
				0.84		
Trihydrogen-1,2,4,5-benzene-tetracarboxylate^{-}	0.07	0.02	0.12			[210]
Hydrogenazelaate^{-}		0.27		1.66	1.31	[211]
Hydrogendiethylene-trioxydiacetate^{-}		0.42		2.13	1.28	[211]
Phenoxyacetate^{-}	0.19	0.08	0.05			[207]
Trihydrogenbutane-tetracarboxylate^{-}		0.22	0.20	1.73	1.14	[129]
Dihydrogencitrate^{-}		0.2	0.1	1.1	1.0	[212]
Glucuronate^{-}		−0.09		1.17	1.03	[213]
Dihydrogen-1,2,3,-propanetricarboxylate^{-}	0.10	0.15	0.10	1.04	0.98	[128]
2-Hydroxypropanoate^{-}	−0.20			1.44	1.30	[79,120,122,214,215]
				1.47	1.33	
				1.42	1.35	
2-Hydroxyacetate^{-}	−0.11			1.48	1.29	[120,122,214]
				1.59	1.33	
Malonate^{2-}	1.31	0.91	1.01	2.39	2.92	[19,123,124,205,216–218]
	0.82	0.85		2.50	2.86	
		0.90		2.35	2.86	
Succinate^{2-}	1.09	0.85	0.86	2.24	2.18	[19,76]
				2.26		
Oxalate^{2-}	1.17	0.88	0.71	3.27	3.58	[195,204,219–222]
		0.82		3.19	3.60	
Maleate^{2-}	1.23	1.18	1.15	2.40	2.30	[19,124]
	0.94					
Malate^{2-}	0.80	0.66	0.7	2.77	2.30	[19,117,118,120]
	0.74^{2}	0.64	0.59	2.55		
			0.54			
Tartrate^{2-}	1.07	1.00	0.75	2.98	2.35	[19,32,203,223]
		0.90		2.89		
		0.75				
Phthalate^{2-}	1.14	1.02	1.12	2.49		[32]
Azelaate^{2-}		0.86		2.28	2.10	[211]
Diethylenetrioxydiacetate^{2-}		1.02		3.65	2.28	[211]
Oxydiacetate^{2-}	1.10	0.71	0.62	4.28	2.51	[19,212]
Hydrogen-5-sulfosalicylate^{2-}		0.65		1.93	1.86	[130]
Hydrogencitrate^{2-}	0.97	0.94	0.74	2.81	2.42	[93,119,212]
				2.79		
Hydrogen-1,2,3,-propanetricarboxylate^{2-}	0.83	0.82	0.78	2.18	2.11	[128]
Dihydrogen-1,2,4,5-benzene-tetracarboxylate^{2-}	0.81	0.67	0.69			[210]
Dihydrogenbutane-tetracarboxylate^{2-}		0.93	0.77	2.79	2.25	[129]
Hydrogen-2,3-dihydroxybenzoate^{2-}	0.75	0.63	0.54			[224]
Citrate^{3-}	1.61	1.54	1.41			[118,119,205,225]
	1.39	1.25	1.14			
		1.43	1.42			
Trihydrogenbenzene-hexacarboxylate^{3-}	0.67	1.54	1.40			[131]
1,2,3,-Propanetricarboxylate^{3-}	1.47	1.40	1.39	3.28	3.26	[128,205]
		1.30		3.17		
Hydrogen-1,2,4,5-benzene-tetracarboxylate^{3-}	1.50	1.25	1.31			[210]
2,3-Dihydroxybenzoate^{3-}	1.67	1.31	1.19			[224]
5-Sulfosalicylate^{3-}		1.40				[130]
Hydrogenbutane-tetracarboxylate^{3-}		1.49	1.33	3.37	3.29	[129]
1,2,4,5-Benzene-tetracarboxylate^{4-}	2.20	2.04	1.96			[210]
Butanetetracarboxylate^{4-}		1.82	1.62	4.50	4.39	[129]
Dihydrogenbenzene-hexacarboxylate^{4-}	1.27	1.88	2.11			[131]
Hydrogenbenzene-hexacarboxylate^{5-}	2.28	2.38	2.46			[131]
Benzenehexacarboxylate^{6-}	2.95	3.06	3.42			[131]

With regard to alkaline earth metal ions, the stability of their complexes is always higher than the corresponding species of alkali metal ions. The trend of stability as a function of atomic number is not always the same, even if for a large number of calcium complexes the stability is the highest. In particular, only the magnesium complexes of malonate and oxalate are significantly more stable than those of calcium. The values of formation constants are strongly dependent on the number of carboxylate donor groups, but the simultaneous presence of hydroxyl or ether groups in the carboxylate molecules may give even a significant contribution to the stability of the complex. If looking at monocarboxylate ligands, the stability is enhanced with 2-hydroxyacetate, 2-hydroxypropanoate, and hydrogendiethylenetrioxydiacetate. If compared with stability of the species formed with the other dicarboxylate ligands, that of calcium complexes with oxydiacetate and diethylenetrioxydiacetate is much higher. Also the stability of $\mathrm{Ca(tartrate)^0}$ can be remarked. The importance of the chelate ring dimension can be derived by comparing the stability of $\mathrm{Ca(oxalate)^0}$ or $\mathrm{Mg(oxalate)^0}$ (five-membered chelate ring) with that of calcium or magnesium complexes of malonate (six-membered) or succinate, maleate or phthalate (seven-membered).

In addition to the data of Table 2 for $\mathrm{Mg^{2+}}$ and $\mathrm{Ca^{2+}}$, in the literature some data are available for $\mathrm{Sr^{2+}}$ and $\mathrm{Ba^{2+}}$. The values of log *K* in the following list refer to the reaction $\mathrm{M^{2+} + L^{z} = ML^{z-2}}$ and to $\mathrm{Sr^{2+}}$ and $\mathrm{Ba^{2+}}$, respectively: monocharged ligands, acetate 0.83 and 0.80 [116,120], propionate 0.80 and 0.71 [120], butyrate 0.73 and 0.68 [120], 2-hydroxypropanoate 0.97 and 0.71 [121,122], 2-hydroxyacetate 1.31 and 1.01 [121,122]. For dicharged ligands, malonate 1.99 and 2.06 [123–125], succinate 2.10 and 2.03 [76,126], maleate 2.35 with $\mathrm{Ba^{2+}}$ [124], oxalate 2.54 with $\mathrm{Sr^{2+}}$ [125], malate 2.12 with $\mathrm{Ba^{2+}}$ [126], tartrate 2.52 with $\mathrm{Ba^{2+}}$ [126,127]. The trend of stability, from $\mathrm{Mg^{2+}}$ to $\mathrm{Ba^{2+}}$, often, but not always, shows a maximum for the stability of calcium complexes and a minimum for complexes of barium.

Most of the carboxylate ligands listed in Table 2 are multidentate and it seems reasonable that they can form bi- (or poly-)nuclear species with the alkali or alkaline earth metal ions. Among the papers reviewed, some also deal with this topic. Binuclear species were reported for citrate, 1,2,3-propanetricarboxylate, 5-sulfosalicylate, butanetetracarboxylate and benzenehexacarboxylate. For citrate, the values of log *K* for the reaction $\mathrm{M^+ + M(cit)^{2-} = M(Mcit)^-}$ are 0.88 ($\mathrm{Li^+}$), 0.80 ($\mathrm{Na^+}$), 0.48 ($\mathrm{K^+}$), 0.38 ($\mathrm{Rb^+}$) and 0.13 ($\mathrm{Cs^+}$) [119]. For 1,2,3-propanetricarboxylate (tca) the values of log *K* for the reaction $\mathrm{M^+ + M(tca)^{2-} = M(Mtca)^-}$ are 0.61 ($\mathrm{Li^+}$), 0.58 ($\mathrm{Na^+}$) and 0.46 ($\mathrm{K^+}$), while the values of log *K* referred to the reaction $\mathrm{M^{2+} + M(tca)^- = M_2(tca)^+}$ are 0.95 and 1.17 for $\mathrm{Ca^{2+}}$ and $\mathrm{Mg^{2+}}$, respectively [128]. With butanetetracarboxylate (btc) the values of log *K* referred the reaction $\mathrm{M^+ + M(btc)^3 = M(Mbtc)^{2-}}$ are 1.62 and 1.58 for $\mathrm{Na^+}$ and $\mathrm{K^+}$, respectively [129]. The value of log *K* for reaction $\mathrm{Na^+ + Na(ssa)^{2-} = Na(Nassa)^-}$ (ssa = sulfosalicylate) is 0.52 [130]. Finally, with benzenehexacarboxylate (mlt) for reaction $\mathrm{M^+ + M(mlt)^{5-} = M(Mmlt)^{4-}}$, log *K* are 1.85 ($\mathrm{Li^+}$), 1.69 ($\mathrm{Na^+}$) and 1.23 ($\mathrm{K^+}$); for reaction $\mathrm{M^+ + M(Hmlt)^{4-} = M(MHmlt)^{3-}}$, log *K* = 1.20 ($\mathrm{Li^+}$), 1.71 ($\mathrm{Na^+}$) and 2.05 ($\mathrm{K^+}$); for reaction $\mathrm{M^+ + M(H_2mlt)^{3-} = M(MH_2mlt)^{2-}}$, log *K* = 1.56 ($\mathrm{Li^+}$), 1.38 ($\mathrm{Na^+}$) and 1.18 ($\mathrm{K^+}$) [131]. Furthermore, both butanetetracarboxylate and benzene-hexacarboxylate show the tendency to bind more than two alkali metal ions, so confirming the importance of the charges involved in the complex formation reaction [129,131].

4.2. Amines

The complexing properties of N-donor ligands towards alkali and alkaline earth metal cations were generally neglected and only few quantitative data are available in the literature [19,132–149]. In particular, no direct evidence for alkali metal ions-N donor ligands interactions was reported, while the formation constants of alkaline earth cations are generally $<10\ \mathrm{mol^{-1}\ L}$. The very weak interactions occurring in these systems make difficult to obtain formation constant values having an acceptable physical significance. Moreover, the formation of these complexes can compete with the weak interactions between the cation and the anion of supporting electrolyte and between the anion of supporting electrolyte and protonated form of N-donor ligand. These considerations explain the difficulty to study these systems. On the other hand, it must be considered that both alkaline earth cations and polyamines have a great importance in natural systems. The concentration of alkaline earth metal cations in natural fluids is generally quite high. Polyamines are found in all living organism, and their concentration becomes quite high in tissues and biological fluids in some pathologies [150–152]. As a consequence, in many systems the formation of $\mathrm{M^{2+}}$-polyamine species can be quite significant.

In spite of this importance, very few studies are reported in the literature and the only papers considering a series of amines in order to draw some model, are those of De Stefano et al. [147] and Kapinos and Sigel [146,148,149]. De Stefano et al. [147] report interactions of a series of linear polyamines $\mathrm{C}_{2(n-1)}\mathrm{N}_n\mathrm{H^+}_{(5n-2)}$ (n = 2. . .5) [ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien), tetraethylenepentamine (tetren) and spermine (sper)] with $\mathrm{Ca^{2+}}$ and $\mathrm{Mg^{2+}}$. For all the $\mathrm{M^{2+}}$-polyamine systems, $\mathrm{MLH_r}^{(r+2)+}$ species (i = 0.1. . .n−1; n = maximum degree of protonation of polyamine L) are formed, generally with stability order $\mathrm{Mg^{2+} > Ca^{2+}}$. For example [147], for $\mathrm{CaL^{2+}}$ and $\mathrm{MgL^{2+}}$ species (L = ethylenediamine) log *K* = 0.15 and 0.38, respectively The stability of magnesium and calcium complexes of polyamines shows a regular increasing trend as a function of the number of amino groups (n), for both unprotonated and protonated species, and it is possible to express the complex stability by the general equation:

$$\log\ K_i^{\mathrm{M}} = b_0 + b_1\, n + b_2 n_{\mathrm{H}}$$

($n_{\mathrm{H}} = i$ = number of protons in the complex species). For the $\mathrm{Mg^{2+}}$ complexes, $b_0 = 0.39$, $b_1 = 0.44$ and $b_2 = -0.16$, and for $\mathrm{Ca^{2+}}$ $b_0 = -0.95$, $b_1 = 0.55$ and $b_2 = -0.05$. The stability of these complexes is not very high, in particular for $\mathrm{Ca^{2+}}$ species, for $n < 3$ and $n_{\mathrm{H}} > n-1$.

Recently, Kapinos and Sigel [149] reported systematic studies on Mg^{2+}-, Ca^{2+}-, Sr^{2+}- and Ba^{2+}-pyridine type ligand systems, studying the influence on binding properties of ligand basicity and of ortho substitution. They found, for 1:1 metal to pyridine ratio: $\log K = -0.20$ (Ba^{2+}), -0.12 (Sr^{2+}), -0.12 (Ca^{2+}) and 0.03 (Mg^{2+}) at $I = 0.5$ mol L^{-1} and 25 °C (Casale et al. [138] reported $\log K = -0.48$ and -0.37 for Ca^{2+} and Mg^{2+}, respectively, at $I = 0$ mol L^{-1} and 25 °C). Stability constants of pyridine derivative ligands resulted linearly related to the acidity of ligand and decreases in the ortho substituted pyridine ligands due to the steric inhibition of the ortho-amino or ortho methyl group: for MgL complexes, $\log K$ values range from 0.02 to 0.07 for simple pyridine derivative and from -0.02 to -0.08 for ortho substituted pyridine type ligands ($I = 0.5$ mol L^{-1}, $t = 25$ °C). Similar studies were reported by Kapinos and Sigel on imidazole [146] and benzimidazole [148] derivatives. For Ca^{2+} and Mg^{2+}-imidazole systems, $\log K = -0.2$ and 0.07 were reported for ML species at $I = 0$ mol L^{-1} and 25 °C [139].

4.3. *Amino acids*

Alkali and alkaline earth cations are involved in numerous biological functions in all living organisms, and most of these functions depend on specialized metal-binding proteins. Therefore, in the last years many papers reported structural studies on the interactions of Li^{+}, Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} [35,153–155] with amino acids. As complexing agents, amino acids show intermediate characteristics between amines and carboxylic ligands probably due to the N,O-chelation, i.e. each aminocarboxylate coordinates *via* both the carboxylate group and the amino group [155]. Beyond the structural studies, few data are reported on the determination of complex formation constants with alkali and alkaline earth metal ions [156–168].

Amino acids, depending on to their structure, can form very weak species with alkali metal cations and weak or, in some cases, fairly stable species with Mg^{2+} and Ca^{2+} [163]. Amino acids with no functional side chain, such as glycine or alanine, can be present in the form HL or L^{-}. In aqueous solution, the anionic species L^{-} interacts with alkaline earth cations. Stability of ML^{+} species is even low, for example for Ca^{2+}-glycine system a mean values of $\log K = 1.4$ can be proposed. The interaction of the neutral amino acid HL is so weak that is reported only in some potentiometric studies: for example for the equilibrium $Ca^{2+} + Hgly = Ca(Hgly)^{2+}$ the values of $\log K = 0.37$ is reported. Amino acids of this kind form very weak species with Na^{+} (for Nagly, $\log K = -0.3$ [163]).

Amino acids containing a side amino or imidazole group (lysine, histidine, aspargine,...) form a very weak species with Na^{+} ($\log K = -0.5$, for histidine) and fairly stable species with Mg^{2+} and Ca^{2+} ($\log K = 1.55$, 0.6 and 0.15, for calcium complexes with histidine, hydrogen-histidine and dihydrogen-histidine, respectively [163]).

Amino acids containing additional carboxylic groups (glutamic, aspartic, iminodiacetic acids,...) form weak species with Na^{+}, and relatively weak species with Mg^{2+} and Ca^{2+} [156,161,166,167]. For reaction of aspartic acid with Na^{+}, it was found $\log K = 0.42$; for Mg^{2+}, $\log K = 2.6$ (mean values at $I = 0.1$ mol L^{-1} and $t = 25$ °C); for Ca^{2+}, $\log K$ ranges from 1.6 to 2.8 ($I = 0.1$ mol L^{-1} and $t = 25$ °C). Stability increases with decreasing the basicity of metal ion. Lumb and Martell [166] reported the stability constants of glutamic (glu) and aspartic (asp) acids with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}: for M(glu) $\log K$ ranges from 1.9 (Mg^{2+}) to 1.28 (Ba^{2+}); for M(asp) $\log K$ comes from 2.43 (Mg^{2+}) to 1.14 (Ba^{2+}). Different protonated species have also been proposed with Ca^{2+} and Mg^{2+} [163]: for the reaction $Ca^{2+} + HL^{-} = Ca(HL)^{+}$ $\log K = 1.7$ and 1.4; for the reaction $Ca^{2+} + H_2L^{0} = Ca(H_2L)^{2+}$ $\log K = 0.8$ and 0.4 for glutamic and aspartic acids, respectively.

The stronger tendency to associate with the calcium and magnesium ions of amino acids with respect to amines is due to the implication of different functional groups and to the formation of chelate rings. Davies and Waind [160] determined the stability of a series of Ca-amino acid systems formulating two hypotheses to explain the different stabilities: (i) the tendency to form chelate structure is rapidly reduced by adding alkyl groups to the glycine molecule and, (ii) the possibility of a tridentate configuration will enhance the tendency to associate with calcium ion.

4.4. *Poly-aminocarboxylate (complexones)*

Poly-aminocarboxylic compounds such as, ethylenediamine-diacetic acid (EDDA), methylimino diethanoic acid (MIDA), nitrilo triacetic acid (NTA), ethylenediamine-tetraacetic acid (EDTA), dioxydiethylenediamine-tetraacetic (EGTA), diethylentriamine-pentaacetic acid (DTPA), triethylenetetramine-hexaacetic acid (TTHA), etc., (the so-called complexones), are, probably, the most used metal chelating agents for industrial, environmental and biomedical applications as well as for analytical purposes. The great interest for this class of compounds is shown by the amount of data reported in the literature and grouped in specific compilations [169–172], in addition to those of more general interest. In spite of that, interactions of complexones with alkali metal ions are in general little investigated, owing to the difficulty to determine the small values of the relative stability constants. However, in order to obtain not conditional protonation constants of the complexones in ionic media containing K^{+} or Na^{+} these interactions have to be taken into account. As suggested by Anderegg [169], a positive correction of $\log(1 + [K^{+}]\ K_{(K-\mathrm{EDTA})}) = 0.21$ for protonation constants of EDTA determined in 0.1 M KNO_3 medium should be considered. An analogous correction was estimated for EDTA protonation constants in Na^{+} medium. For this reason, on the basis of the pioneering work of Schwarzenbach et al. [173] and Schwarzenbach and Ackerman [174], some accurate measurements were made on the stability of alkali metal complexes with EDTA and NTA [175–178]. A critical evaluation of the formation constants was reported by Anderegg [169,170]. The average values of $\log K$ for ML species ($I = 0.1$ mol L^{-1} and $t = 25$ °C) are as follows: 2.50, 1.3 and 0.7 for NTA-Li^{+}/Na^{+}/K^{+} systems and 2.85, 1.75 and 0.7 for EDTA-Li^{+}/Na^{+}/K^{+} systems. As expected for an ion association model, there is a trend of decreasing stability with the cation ionic radius increasing. The values of stability constants for NTA-Li^+/Na^+/K^+ system are in good accordance with those reported later by Daniele et al. [98]. A value of $\log K = 2.70$ was recently reported by Felmy and Mason [179] for the formation of EDTA/Na^+ complex at $t = 22–23\,°C$ and $I = 0\ mol\ L^{-1}$. Stability constants of alkali and alkaline earth metal EDTA complexes were also related to the solubility of the species according to the following empirical relationship [180]: $\log S + 3.6pH_{sat} = 23.3–1.13 \log K$. Interaction of alkali metal ions with other complexones was less investigated. The formation of a species DTPA-Li^+ was reported by Wanninen [181] with a $\log K = 3.1$ ($I = 0.1\ mol\ L^{-1}$ and $t = 25\,°C$). Kumar and Nigam [182] gave a little reliable value of $\log K = 1.0$ for the species TTHA-Na^+ in $0.5\ mol\ L^{-1}$ KNO_3 medium at $t = 25\,°C$.

More recently, a study on the acid-base behaviour of DTPA and TTHA in multicomponent solution containing alkali and alkaline earth metal ions, as major components of natural waters, and at different ionic strengths was reported by De Stefano et al. [183]. The lowering of protonation constants of DTPA and TTHA in NaCl medium, with respect to those calculated in Et_4NI and Me_4NCl, was interpreted in terms of NaDTPA and NaTTHA weak complex formation, according to an association model. The investigation carried out in a wide pH range allows the authors to report the formation of differently protonated sodium species (NaH_rL_q) with $r = 0$ to 4 and 0 to 5 for DTPA and TTHA systems, respectively. Log K for all the species were given at $I = 0\ mol\ L^{-1}$ and range from 2.5 and 2.8 to −0.4 and −0.5 for NaL and $Na(H_4L)$ and $Na(H_5L)$ in the DTPA and TTHA systems, respectively. Authors also report the formation of a homobinuclear species: for the reaction $Na^+ + NaL^{z+1} = Na(NaL)^{z+2}$, $\log K = 1.6$ and 2.0 for DTPA and TTHA respectively, confirming the hypothesis already expressed [171] on the formation of such a species in TTHA system. Crea et al. [184] extended this investigation to other complexones, NTA, EGTA and EDTA. In addition to the species already reported [183] for DTPA and TTHA systems, analogous NaH_rL_q complexes were found for EDTA and EGTA systems, together with the binuclear Na(NaEGTA) and Na(NaHEGTA) species with $\log K = 1.2$ and 0.2, respectively. In these two last works the formation of ternary species NaMgL and NaCaL obtained in NaCl–$MgCl_2$ and NaCl–$CaCl_2$ mixtures, is also reported for the first time, with the following $\log K$ values for the reaction $Na^+ + ML$ (M = alkaline earth metal ion, L = complexone): Na(CaEGTA) = 0.65, Na(CaDTPA) = 0.68, Na(CaTTHA) = 2.1, Na(MgEGTA) = 0.2, Na(MgDTPA) = 0.80, Na(MgTTHA) = 2.0.

No data are reported for other complexones, such as MIDA and EDDA.

4.5. Nucleotides

Stability data on alkali nucleotide weak complexes were reported in a more general review on nucleotide metal interaction by Smith et al. [185]. Formation constant of ML species is: for adenosine-5′-monophosphate^{2-} (AMP), $\log K = 0.98$, 0.83 and 0.6 [89] with Li^+, Na^+ and K^+, respectively; for adenosine-5′-diphosphate^{3-} (ADP), $\log K = 1.71$ (Li^+), 1.39 (Na^+) and 1.29 (K^+) [89,186]; for adenosine-5′-triphosphate^{4-} (ATP), $\log K = 2.43$ (Li^+), 1.98 (Na^+), 1.87 (K^+), 1.98 (Rb^+) and 1.94 (Cs^+) [89,175,187,188]; for adenosine-5′-tetraphosphate^{5-} (AQP), $\log K = 2.85$ (Li^+), 2.18 (Na^+) and 2.04 (K^+) [89]. The trend of stability, with respect the different alkali metals and the nucleotides, is the same already pointed out for the most part of the ligands examined in this review. In other words, the highest stability is in correspondence of the highest metal ion charge/radius ratio or the highest ligand charge. For Li^+–ATP a binuclear species was also reported with $\log K = 1.91$ which refers to the reaction $Li^+ + Li(ATP)^{3-} = Li(LiATP)^{2-}$ [187].

5. Applications to natural multi-component solutions

5.1. Weak interactions between major components of seawater: the marine salt

The weak interactions of alkali and alkaline earth cations play a very important role in multi-component solutions such as seawater. As is well known, the highest contribution (>99.5%) to the seawater salinity is given by the 11 conservative components, i.e. Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Cl^-, Br^-, $B(OH)_3$, F^-, $HCO_3{}^-$ whose concentrations (mol/kg of seawater) at S = 35‰ (S = salinity), pH = 8.1 and $t = 25\,°C$ are: 0.4691 (Na^+), 0.01021 (K^+), 0.01028 (Ca^{2+}), 0.05282 (Mg^{2+}), 0.00009 (Sr^{2+}), 0.54615 (Cl^-), 0.02824 ($SO_4{}^{2-}$), 0.00084 (Br^-), 0.00041 ($B(OH)_3$), 0.00007 (F^-) and 0.00205 ($HCO_3{}^-$) [189].

As reported in the previous paragraphs, different very weak, weak or quite stable species are formed between the ionic components of seawater [NaCl, KCl, $MgCl^+$, $CaCl^+$, $Na(SO_4)^-$, $Mg(OH)^+$, $Mg(SO_4)$ and $Ca(SO_4)$] making elaborate the speciation studies. To overcome this difficulty, De Stefano et al. [190] proposed a simplified model according to which the major cations of seawater (Na^+, K^+, Ca^{2+} and Mg^{2+}) are represented by a single cation B^{z+} and the anions (Cl^- and $SO_4{}^{2-}$) by a single anion A^{z-}. Therefore, the six major components of the artificial seawater are expressed as a single salt, BA, having mean concentration $C_{BA} = 1/2 \sum_i c_i = 0.5751\ mol\ L^{-1}$ or $0.5824\ mol\ kg^{-1}$ (with c_i = concentration of anions and cations of artificial seawater 35‰ salinity) and charge $z\pm = (I/C_{BA})^{1/2} = 1.117\pm$ (with $I = 0.717\ mol\ L^{-1}$ or $0.726\ mol\ kg^{-1}$). The internal interactions between the components of the seawater ionic medium provide the formation of only three weak species: the BA ($\log K = -0.03$), HA ($\log K = 0.24$), and B(OH) ($B^{z+} = B(OH)^{(z-1)} + H^+$: $\log K = -12.75$). Cationic and anionic components of the single sea-salt show an intermediate strength of interaction between that of alkali and alkaline earth metal ions with regard to both the internal interactions and those with components of acid-base systems under study. The use of this model allows to evaluate the cumulative binding capacity of inorganic components of seawater, as shown in a comprehensive study on the acid-base behaviour of some classes of ligands, metal and organometallic cations in artificial seawater [191].

De Robertis et al. [192] reported a systematic study on the protonation and association of low molecular weight mono to hexa carboxylic ligands with major components of seawater. The interactions with cation $B^{1.117+}$ of single seawater salt lead to the formation of B(L) species for acetate; B(L) and B(HL) species for all the dicarboxylates; B(L), B(HL), B(H_2L) and B_2(L) for tricarboxylates; B(L), B(HL), B(H_2L), B(H_3L) and B_2L for tetra and hexa carboxylates. Results obtained by the authors showed that the values of formation constants are strictly related to the number of carboxylic groups involved in the coordination, i.e. to the charge of the ligand. Authors also report the simple relationship between log K value and the number (n) of carboxylic binding groups, $\log K = 0.37\, n^{3/2}$, useful to predict the values of B-carboxylates association constants in the range $1 \leq n \leq 5$.

De Stefano et al. [193] reported a comprehensive investigation on the protonation and association of di-/penta-amines (am) with the single salt BA. The formation of $(\mathrm{amH_i})\mathrm{A}^{(\mathrm{i}-1.117)}$ and $(\mathrm{am})\mathrm{B}^{1.117+}$ species was formulated. In the investigated systems, values of log K range for all (am)H_iA species (i = 1 to 5) from 0.5 to 3.6 and for B(am) species from 0.14 to 0.42. $\log K_{\mathrm{B(am)}}$ constant was related [$\mathrm{Log}\, K_{\mathrm{B}} = 0.27 \log K_{\mathrm{MgCa}}$] to a mean formation constant for alkaline earth metal species, K_{MgCa}, which takes into account the concentration of Mg^{2+} and Ca^{2+} in the artificial seawater [$K_{\mathrm{MgCa}} = (K_{\mathrm{Mg}}\, C_{\mathrm{Mg}} + K_{\mathrm{Ca}}\, C_{\mathrm{ca}})/(C_{\mathrm{Mg}} + C_{\mathrm{ca}})$]. Log K values determined for the different MgCa-amine systems were: 0.35, 0.87, 1.39, 1.71, 1.63 for en, dien, trien, tetren and sper, respectively.

The use of single salt approximation for amino acid equilibrium studies [164] showed the formation of B(L), B(HL) and (H_2L)A (for L = glycine and alanine); B(L), B(HL), (H_2L)A and (H_3L)A (for L = histidine) and B(L), B(HL) and B(H_2L) (for L = glutamic and aspartic acids). The stability of BL and B(HL) species for glycine, alanine and histidine systems is very similar with mean values of log K = 0.75 and 0.25, respectively.

A study carried out on the interaction of phenol and some its derivative in artificial seawater [194] showed the formation of $\mathrm{BL}^{0.117+}$ species with a mean stability of 1.3 mol^{-1} L. This stability is somewhat lower than that of mono-carboxylic ligands, but is of same magnitude order.

5.2. Other applications

The same approach adopted to model seawater can be adopted for *urine* [195], whose electrolyte content can be modelled according to an equilibrium principle to obtain the value of free calcium ion available to form scarcely soluble oxalate or phosphate salts causing renal calculosis. Ion pairs concur to establish the amount of a free metal ion in a real fluid and, moreover, to define its correct value of ionic strength, since the ion pairs formation lowers the ions content and, consequently, the ionic strength values. For urine, reference values for pH are 5.0–7.0 and main electrolytes are: H^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, oxalate, citrate, hydrogenphosphate, chloride and sulfate. Ionic strength is very often >0.1 mol L^{-1} and can reach 0.3–0.4 mol L^{-1}. Other components as protonated amines, amino acids and urea were also considered. The solubility at 37 °C and different ionic strengths of both calcium oxalate monohydrate and calcium hydrogenphosphate dihydrate were studied [196] to evaluate the saturation state of urine. Coupling the output of the chemical model of the ionic compounds of urine with the solubility data one can foresee the thermodynamic tendency of the litho-genetic compound precipitation. Urea is the only non-ionic compound considered [197]: the amount in urine is high and it might indirectly influence the overall equilibrium status affecting the protonation and formation constants values. The chemical model consists in 52 equilibrium reactions – including protonations and ion pair formation – and allows to calculate the free calcium ion whose value has also been verified for various urine samples *via* potentiometric measurements with a calcium(II)-sensitive electrode. Another validation of the model was achieved *via* solubility measurements [198].

A speciation model [199] – involving 17 reactants and 77 equilibria (protonation and complex formation equilibria, supporting electrolyte ($(C_2H_5)_4I$) – was built to interpret in terms of chemical equilibria the pH of wine. This model allows as well to obtain a reliable estimation of the free concentration of both Ca^{2+} and K^+, useful to solve technological problems related to many steps of the wine production and evolution. Although at pH around 3 the ion pair formation process is not so important, it can be underlined that wine is a sulfate-rich beverage and K^+, Ca^{2+} and Mg^{2+} are largely involved in sulfate ion pairs. Precipitation of scarcely soluble salts of oenological interest, as calcium tartrate or potassium hydrogen-tartrate, can be foreseen, being able to distinguish total from free concentration of both Ca^{2+} and K^+.

Ion pair formation appears to play an important role in percutaneous absorption of diclofenac (2-[2-(2,6-dichlorophenyl)aminophenyl]ethanoic acid) [200]. Industry is interested in the role played by ion pairs for citric acid partitioning between aqueous and organic phases [201,202].

6. Discussion and conclusions

6.1. On the reliability of formation constants

As briefly outlined above, pH-metric measurements were widely employed in determining the stability constants of weak complexes, by using tetralkylammonium salts as ionic medium. Some authors [118,129,131,195,203–206], however, had recourse to other ion-selective electrodes, with the aim of obtaining further specific information about complex formation. Among the different reports, one paper [205] deals with the weak complex formation, only by employing the potentiometric technique with ion-selective electrodes, at variable ionic strength. Furthermore, since a significant variation of ionic strength during the experiment might be a possible source of error in this type of determinations, an ISE-Na^+ electrode was employed in experiments at constant ionic medium and ionic strength [206]. The results so obtained for sodium complexes of malonate, phthalate, citrate, NTA and EDTA are not affected by errors in activity coefficient values and can be compared with those previously reported for the same species. There is a good agreement between the log K values determined with ISE-Na^+ at constant ionic strength and the previous ones (pH-metric or with other ISE at variable ionic strength) for the ligands considered, so confirming the reliability of pH-metric technique for a correct study of weak complex formation.

6.2. Calculations and general considerations

As expected, being the stability of weak alkali and alkaline earth metal complexes mainly due to electrostatic interaction, simple relationships can be found between log K and z (z = charge of anion). By considering altogether carboxylate complexes we found the following very simple equations:

$$\log\ K = \frac{1}{2}|z| + \frac{A}{|z|} \qquad (10)$$

for Li^+, Na^+ and K^+, and

$$\log\ K = |z| + \frac{B}{|z|} \qquad (11)$$

for Mg^{2+} and Ca^{2+}. Fitting results are: $A = -0.243$, -0.300 and -0.432, for Li^+, Na^+ and K^+, respectively, with mean deviation in the formation constant of 0.15 log units; $B = 0.37$ and 0.69 for Mg^{2+} and Ca^{2+}, respectively, with mean deviation 0.35. Some considerations can be done about these results.

(i) Eq. (10) has quite a good predictive power since rarely the formation constants of alkali metal complexes can be obtained with a precision better than ±0.1 log units. For alkaline earth metal complexes the mean deviation is significantly higher, but Eq. (11) is still useful for guessing purpose.

(ii) Values of A and B parameters confirm the stability general trend of these carboxylate complexes:

$$Li^+ > Na^+ > K^+; \quad Ca^{2+} > Mg^{2+}$$

(iii) Eqs. (10) and (11) also account for the lowering of the above trends with increasing values of $|z|$. The difference $\log K_{Li} - \log K_K$ is 0.19, 0.05 and 0.03, for $|z| = 1$, 4 and 6, respectively. Analogously, $\log K_{Ca} - \log K_{Mg} = 0.36$, 0.18 and 0.12 for $|z| = 1$, 2 and 3, respectively. This means that the ratio charge/mass is less important for large anions. For large inorganic anions this behaviour is more evident.

For alkali metal complexes, it is also possible to calculate mean values of formation constants for all the complexes considered in this review, as reported in Fig. 1. Confidence intervals are obviously larger than for carboxylate complexes, but mean values are still significant for predictive purposes. These mean values can be fitted to Eq. (10), with $A = -0.26$, -0.30 and -0.45, for Li^+, Na^+ and K^+, respectively. It is noticeable that A values are very similar to those obtained for carboxylate complexes. A slightly better fit is obtained by using a polynomial equation $\log K = p_0 + \Sigma p_i\,|z|^i$. In Table 3 we report mean values and calculated values obtained by Eq. (10).

Enthalpy changes for the formation of alkali and alkaline earth metal complexes are generally low and positive [19,27,29,72,76,91,92,97,98,124,135,187,207,208], indicating that the main contribution to the stability is entropic in nature. The following general considerations can be made:

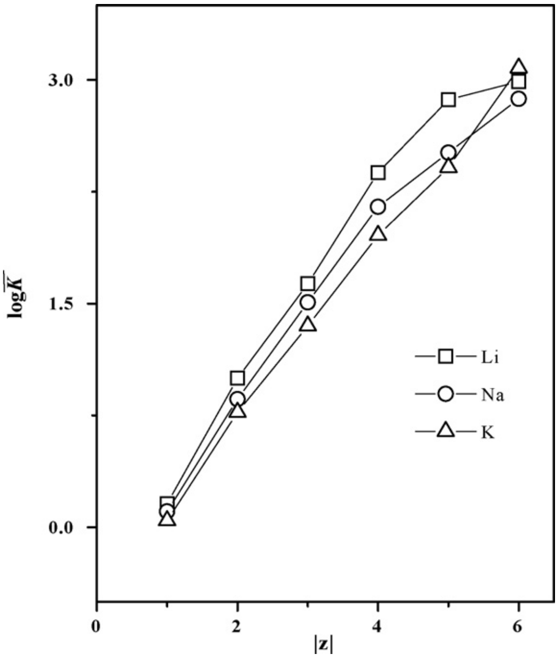

Fig. 1. Mean values of formation constants for Li^+, Na^+ and K^+ complexes of organic and inorganic (poly)anions, at $I = 0$ mol L^{-1} and $t = 25$ °C, vs. anion charge z.

(i) The dispersion of ΔH^0 values is higher than that of log K, and this is due to the reasons: the term $T\Delta S^0$ is more selective than ΔG^0, and, the reported values of enthalpy changes are affected by large errors.

(ii) $T\Delta S^0$ values, for alkali metal complexes, are quite similar, independently of the charge of anions, whilst alkaline earth metal complexes show a significantly higher $T\Delta S^0$ contribution.

(iii) For all the Li^+, Na^+ and K^+ weak species it is possible to calculate a mean value, namely $T\Delta S^0 = 8 \pm 2$ kJ mol^{-1}.

Table 3
Mean values of formation constants of Li^+, Na^+ and K^+ complexes of poly(anions) having different charges (z), at $I = 0$ mol L^{-1} and $t = 25$ °C

M	z	$\log \bar{K}$	Standard (error)	$\log \bar{K}_{calcd}$[a]
Li^+	−1	0.16	0.04	0.25
	−2	1.00	0.04	0.88
	−3	1.63	0.2	1.42
	−4	2.38	0.3	1.94
	−5	2.87	0.3	2.45
	−6	2.99	0.2	2.96
Na^+	−1	0.11	0.06	0.20
	−2	0.86	0.03	0.85
	−3	1.51	0.06	1.40
	−4	2.15	0.1	1.92
	−5	2.51	0.2	2.44
	−6	2.87	0.2	2.95
K^+	−1	0.04	0.07	0.05
	−2	0.77	0.04	0.77
	−3	1.35	0.03	1.35
	−4	1.96	0.07	1.89
	−5	2.41	0.2	2.41
	−6	3.08	0.3	2.92

[a] Calculated from Eq. (10).

(iv) Only few data are available for Mg^{2+} and Ca^{2+} species, and this does not allow to give general conclusions.

6.3. Conclusions

Weak complex formation by alkali and alkaline earth metal ions was widely investigated by a great number of authors who have paid attention to the various aspects of this topic, such as detection of species in solution and their stoichiometry, determination of formation constants, estimation of thermodynamic parameters. Although potentiometry is the technique employed by the most part of investigators, some researchers had recourse to NMR, calorimetry, dilatometry, circular dichroism and mass spectrometry, often with the aim of confirming the results coming from potentiometric measurements.

The stability of these complexes is mainly due to electrostatic interactions and therefore increases with raising the charge of reactants. A relevant consequence of this aspect is that the stability constant of a species can be foreseen with a good approximation. The existence of specific effects concurring to the stability is rare. The relevance of these species, in spite of their weakness, is related to the high concentration of alkali and alkaline earth metal ions in all natural (and often also in artificial) chemical systems. However, several stability data must be checked by different experimental techniques, and the relative ΔH values have to be determined by direct methods (calorimetry).

Some literature applications to real systems suggest that the building of chemical model for the interpretation of the behaviour of natural or artificial fluids may be much improved if the formation of these complexes is considered too.

References

[1] D.A. Phipps, in: G. Berthon (Ed.), Handbook of Metal Ligand-Interaction in Biological Fluids. Part 2, Bioinorganic Medicine, 1995, p. 89.

[2] K. Aoki (Ed.), Metal ion in biological systems, vol. 32. Interactions of Metal Ions With Nucleotides, Nucleic Acids and Their Derivatives, 1996, p. 91.

[3] D. Midgley, Chem. Soc. Rev. 4 (1975) 549.

[4] N.S. Poonia, A.V. Bajaj, Chem. Rev. 79 (1979) 389.

[5] N.V. Sidgwick, J. Chem. Soc. (1925) 209.

[6] L.G. Sillén, A.E. Martell, Stability Constants of Metal Ion Complexes. Special Publ. 17, The Chemical Society, Wiley, London, 1964.

[7] L.G. Sillén, A.E. Martell, Stability Constants of Metal Ion Complexes. Supplement Special Publ. 25, The Chemical Society, Wiley, London, 1964.

[8] R.M. Smith, A.E. Martell, Critical Stability Constants, vol. 1. Amino Acids, Plenum Press, New York, 1974.

[9] R.M. Smith, A.E. Martell, Critical Stability Constants, vol. 2. Amines, Plenum Press, New York, 1975.

[10] R.M. Smith, A.E. Martell, Critical Stability Constants, vol. 4. Inorganic Complexes, Plenum Press, New York, 1976.

[11] R.M. Smith, A.E. Martell, Critical Stability Constants, vol. 3. Other Organic Ligands, Plenum Press, New York, 1977.

[12] D.D. Perrin, Stability Constants of Metal Ions Complexes, Part B: Organic Ligands, IUPAC Chemical Data Series No. 22, Pergamon Press, Oxford, 1979.

[13] E. Hogfeldt, Stability Constants of Metal-Ion Complexes. Part A: Inorganic Ligands, IUPAC Chemical Data Series, No. 21, Pergamon Press, Oxford, 1982.

[14] R.M. Smith, A.E. Martell, Critical Stability Constants, vol. 5. First Supplement, Plenum Press, New York, 1982.

[15] R.M. Smith, A.E. Martell, Critical Stability Constants, vol. 6. Second Supplement, Plenum Press, New York, 1989.

[16] P.M. May, K. Murray, J. Chem. Eng. Data 46 (2001) 1035.

[17] L. Pettit, K.J. Powell, The IUPAC Stability Constants Database, Academic Software, 2001.

[18] A.E. Martell, R.M. Smith, R.J. Motekaitis, Critically Selected Stability Constants of Metal Complexes, National Institute of Standard and Technology, NIST, PC-based Database, Gaithersburg, 2004.

[19] P.G. Daniele, A. De Robertis, C. De Stefano, S. Sammartano, C. Rigano, J. Chem. Soc. Dalton Trans. (1985) 2353.

[20] Y. Marcus, G. Hefter, Chem. Rev. 106 (2006) 4585.

[21] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations, John Wiley & sons, New York, 1976.

[22] F.G.R. Gimblett, C.B. Monk, Trans. Faraday Soc. 50 (1954) 965.

[23] G. Grossmann, K.A. Burkov, G. Hagele, L.A. Myund, S. Hermens, C. Verwey, S.M. Arat-ool, Inorg. Chim. Acta 357 (2004) 797.

[24] K. Popov, L.H.J. Lajunen, A. Popov, H. Ronkkomaki, M. Hannu-Kuure, A. Vendilo, Inorg. Chem. Comm. 5 (2002) 223.

[25] K. Akiko, O. Takao, Z. Naturforsch. 53a (1998) 77.

[26] V. Cucinotta, P.G. Daniele, C. Rigano, S. Sammartano, Inorg. Chim. Acta 56 (1981) L43.

[27] G. Arena, R. Calì, M. Grasso, S. Musumeci, S. Sammartano, C. Rigano, Thermochim. Acta 36 (1980) 329.

[28] T.E. Zelenina, O.Y. Zelenin, Russ. J. Coord. Chem. 31 (2005) 235.

[29] R.M. Izatt, D. Eatough, J.J. Christensen, C.H. Bartholomew, J. Chem. Soc. (A) (1969) 45.

[30] J.M. Austin, A.D. Mair, J. Phys. Chem. 66 (1962) 519.

[31] P.G. Daniele, C. De Stefano, O. Giuffrè, E. Prenesti, S. Sammartano, Talanta 54 (2001) 25.

[32] P.G. Daniele, C. De Stefano, O. Giuffrè, E. Prenesti, S. Sammartano, J. Chem. Soc. Dalton Trans. (2002) 435.

[33] M. Titta, M. Leskea, E. Nykanen, P. Soininen, L. Niinisto, Thermoch. Acta 256 (1995) 47.

[34] J.A. Stone, D. Vukomanovic, Inter. J. Mass Spectr. 210 (2001) 341.

[35] R.M. Moision, P.B. Armentrout, J. Phys. Chem. A 110 (2006) 3933.

[36] X. Xuan, J. Wang, H. Wang, Eletrochim. Acta 50 (2005) 4196.

[37] A. De Robertis, S. Sammartano, C. Rigano, Thermochim. Acta 74 (1984) 343.

[38] H.S. Harned, B.B. Owen, The Physical Chemistry of Electrolyte Solutions, Reinhold Pub. Corp, New York, 1958.

[39] P. Gans, A. Sabatini, A. Vacca, Talanta 43 (1996) 1739.

[40] A. De Robertis, C. De Stefano, S. Sammartano, C. Rigano, Talanta 34 (1987) 933.

[41] C. De Stefano, C. Foti, O. Giuffrè, P. Mineo, C. Rigano, S. Sammartano, Ann. Chim. (Rome) 86 (1996) 257.

[42] K.S. Pitzer, J. Phys. Chem. 77 (1973) 268.

[43] L.A. Bromley, AIChE J. 19 (1973) 313.

[44] L. Ciavatta, Ann. Chim. 70 (1980) 551.

[45] I. Grenthe, I. Puigdomenech, Modelling in Aquatic Chemistry, OECD, Paris, 1997.

[46] J.N. Brönsted, J. Am. Chem. Soc. 44 (1922) 877.

[47] G. Scatchard, Chem. Rev. 19 (1936) 309.

[48] E.A. Guggenheim, J.C. Turgeon, Trans. Faraday Soc. 51 (1955) 747.

[49] C. Rey-Castro, R. Castro-Varela, R. Herrero, M.E. Sastre de Vicente, Talanta 60 (2003) 93.

[50] R.A. Robinson, H.S. Harned, Chem. Rev. 28 (1941) 419.

[51] H.S. Harned, H.R. Copson, J. Am. Chem. Soc. 55 (1933) 2206.

[52] H.S. Harned, J.G. Donelson, J. Am. Chem. Soc. 59 (1937) 1280.

[53] H.S. Harned, W.J. Hamer, J. Am. Chem. Soc. 55 (1933) 2194.

[54] H.S. Harned, G.E. Mannweiler, J. Am. Chem. Soc. 57 (1935) 1873.

[55] H.S. Harned, O.E. Schupp, J. Am. Chem. Soc. 52 (1930) 3892.

[56] L.S. Darken, H.F. Meier, J. Am. Chem. Soc. 64 (1942) 621.

[57] M. Spiro, Trans. Faraday Soc. 51 (1959) 1746.

[58] P.G. Daniele, M. Grasso, C. Rigano, S. Sammartano, Ann. Chim. (Rome) 73 (1983) 495.

[59] H. Ohtaki, Acta Chem. Scand. 18 (1964) 521.

[60] D.A. Palmer, D.J. Wesolowski, J. Sol. Chem. 26 (1997) 217.
[61] D. Lewis, Acta Chem. Scand. 17 (1963) 1891.
[62] F.J. Millero, J. Phys. Chem. 74 (1970) 356.
[63] K. Johnson, R.M. Pytkowicz, Am. J. Sci. 278 (1978) 1428.
[64] A. De Robertis, C. De Stefano, Ann. Chim. (Rome) 88 (1998) 103.
[65] A. De Robertis, C. Rigano, S. Sammartano, O. Zerbinati, Thermochim. Acta 115 (1987) 241.
[66] A.A. Reznikov, V.A. Shaposhnik, Russ. J. Phys. Chem. 81 (2007) 179.
[67] J. Zhou, X.-H. Lu, Y.-R. Wang, J. Shi, W.-C. Wang, J. Chin. Chem. Soc. 59 (2001) 2070.
[68] R. Heyrovska, J. Electrochem. Soc. 143 (1996) 1789.
[69] E.C. Righellato, C.W. Davies, Trans. Faraday Soc. 26 (1930) 592.
[70] H.W. Jones, C.B. Monk, Trans. Faraday Society 48 (1952) 929.
[71] V.S.K. Nair, G.H. Nancollas, J. Chem. Soc. (1958) 3706.
[72] R.M. Izatt, D. Eatough, J.J. Christensen, C.H. Bartholomew, J. Chem. Soc. (A) (1969) 47.
[73] F.H. Fisher, A.P. Fox, J. Sol. Chem. 4 (1975) 225.
[74] F.H. Fisher, A.P. Fox, J. Sol. Chem. 6 (1977) 641.
[75] P.G. Daniele, C. Rigano, S. Sammartano, Inorg. Chim. Acta 63 (1982) 267.
[76] A. De Robertis, C. De Stefano, R. Scarcella, C. Rigano, Thermochim. Acta 80 (1984) 197.
[77] C. De Stefano, C. Rigano, S. Sammartano, R. Scarcella, J. Chem. Res. (S) (1988) 372.
[78] A. De Robertis, C. De Stefano, S. Sammartano, A. Gianguzza, Chem. Spec. Bioavail. 6 (1994) 65.
[79] A.R. Felmy, D. Rai, J.E. Amonette, J. Sol. Chem. 19 (1990) 175.
[80] F.P. Daly, C.W. Brown, D.R. Kester, J. Phys. Chem. 76 (1972) 3664.
[81] R.M. Garrels, M.E. Thompson, Am. J. Sci. 260 (1962) 57.
[82] J.N. Butler, R. Huston, J. Phys. Chem. 74 (1970) 2976.
[83] R.M. Pytkowicz, J.E. Hawley, Limnol. Oceanogr. 19 (1974) 223.
[84] S.G. Capewell, G. Hefter, P.M. May, J. Sol. Chem. 27 (1998) 865.
[85] R.N. Roy, L.N. Roy, K.M. Vogel, C. Porter-Moore, T. Pearson, C.E. Good, F.J. Millero, D.M. Campbell, Mar. Chem. 44 (1993) 249.
[86] F.J. Mojica Prieto, F.J. Millero, Geochim. Cosmochim. Acta 66 (2002) 2529.
[87] F. Crea, C. De Stefano, A. Gianguzza, D. Piazzese, S. Sammartano, Talanta 68 (2006) 1102.
[88] D.A. Palmer, R.V. Eldik, Chem. Rev. 83 (1983) 651.
[89] R.M. Smith, R.A. Alberty, J. Phys. Chem. 60 (1956) 180.
[90] A.W. Taylor, A.W. Frazier, E.L. Gurney, J.P. Smith, Trans. Faraday Soc. 59 (1963) 1585.
[91] A. Chugtai, R. Marshall, G.H. Nancollas, J. Phys. Chem. 72 (1968) 208.
[92] P.G. Daniele, A. De Robertis, C. De Stefano, A. Gianguzza, S. Sammartano, J. Solution Chem. 20 (1991) 495.
[93] L. Ciavatta, M. Iuliano, R. Porto, Ann. Chim. (Rome) 81 (1991) 243.
[94] L. Ciavatta, M. Iuliano, R. Porto, Ann. Chim. (Rome) 84 (1994) 95.
[95] C. De Stefano, C. Foti, A. Gianguzza, D. Piazzese, Chem. Spec. Bioavail. 10 (1998) 19.
[96] R.M. Smith, R.A. Alberty, J. Am. Chem. Soc. 78 (1956) 2376.
[97] V.P. Vasil'ev, S.A. Aleksandrova, Zhur. Neorg. Khim. 18 (1973) 2055.
[98] P.G. Daniele, C. Rigano, S. Sammartano, Anal. Chem. 57 (1985) 2956.
[99] C. De Stefano, C. Foti, A. Gianguzza, J. Chem. Res. 464 (1994) 2639.
[100] J.I. Watters, S.M. Lambert, E.D. Loughran, J. Am. Chem. Soc. 79 (1957) 3651.
[101] A.M. Bond, G.T. Hefter, Critical survey of stability constants and related thermodynamic data of fluoride complexes in aqueous solution, N. IUPAC Chemical Data Series, Critical evaluation of equilibrium constants in solution. Part A: stability constants of metal complexes, Pergamon press, Oxford, 1980.
[102] G.R. Miller, D.R. Kester, Mar. Chem. 4 (1976) 67.
[103] B. Elgquist, J. Inorg. Nucl. Chem. 32 (1970) 937.
[104] A. De Robertis, C. Rigano, S. Sammartano, Ann. Chim. (Rome) 74 (1984) 33.
[105] S. Capone, A. De Robertis, C. De Stefano, R. Scarcella, J. Chem. Res. (S) (1986) 412.
[106] S. Capone, A. De Robertis, S. Sammartano, C. Rigano, Thermochim. Acta 102 (1986) 1.
[107] M.T. Beck, Chemistry of Complex Equilibria, Van Nostrand Reinhold, London, 1970.
[108] W.A. Eaton, P. George, G.I.H. Hanania, J. Phys. Chem. 71 (1967) 2016.
[109] Y.I. Rutkovskii, V.E. Mironov, Zhur. neorg. Khim. 12 (1967) 3287.
[110] J.M. Pratt, J.P. Williams, J. Chem. Soc. (A) (1967) 1291.
[111] N. Li, O. Wahlberg, Acta Chem. Scand. 43 (1989) 401.
[112] C. De Stefano, D. Milea, A. Pettignano, S. Sammartano, Anal. Bioanal. Chem. 376 (2003) 1030.
[113] J. Torres, S. Dominguez, M.F. Cerda, G. Obal, A. Mederos, R.F. Irvine, A. Diaz, C. Kremer, J. Inorg. Biochem. 99 (2005) 828.
[114] F. Crea, P. Crea, C. De Stefano, D. Milea, S. Sammartano, J. Mol. Liquids, submitted.
[115] H. Bieth, G. Schlewer, B. Spiess, J. Inorg. Biochem. 41 (1991) 41.
[116] A. De Robertis, C. De Stefano, C. Rigano, S. Sammartano, R. Scarcella, J. Chem. Res. (S) (1985) 42.
[117] L.E. Erickson, J.A. Denbo, J. Phys. Chem. 67 (1963) 707.
[118] G.A. Rechnitz, S.B. Zamochnick, Talanta 11 (1964) 1061.
[119] P.G. Daniele, A. De Robertis, C. De Stefano, A. Gianguzza, S. Sammartano, J. Chem. Res. 300 (1990) 2316.
[120] R.K. Cannan, A. Kibrick, J. Am. Chem. Soc. 60 (1938) 2314.
[121] C.A. Colmar-Porter, C.B. Monk, J. Chem. Soc. (1952) 4363.
[122] P.B. Davies, C.B. Monk, Trans. Faraday Soc. 50 (1954) 128.
[123] R.H. Jones, D.I. Stock, J. Chem. Soc. (1962) 306.
[124] U.K. Klaning, O. Osterby, J. Chem. Soc. Faraday Trans. 72 (1976) 513.
[125] W.J. Harrison, G.D. Thyne, Geochim. Cosmochim. Acta 56 (1992) 565.
[126] J. Schubert, J. Am. Chem. Soc. 76 (1954) 3442.
[127] S.H. Laurie, C.B. Monk, J. Chem. Soc. (1963) 3343.
[128] C. De Stefano, C. Foti, A. Gianguzza, Talanta 41 (1994) 1715.
[129] A. De Robertis, C. Foti, A. Gianguzza, Ann. Chim. (Rome) 83 (1993) 485.
[130] C. Foti, A. Gianguzza, D. Piazzese, S. Orecchio, Ann. Chim. (Rome) 92 (2002) 551.
[131] A. De Robertis, C. De Stefano, C. Foti, Ann. Chim. (Rome) 86 (1996) 155.
[132] J. Bjerrum, Metal Ammine Formation in Aqueous Solution, P. Haase and son, Copenhagen, 1957.
[133] W.E. Hatfield, J.T. Yoke, Inorg. Chem. 1 (1962) 463.
[134] K.S. Rajan, J.M. Davis, Colburn, J. Neurochem. 18 (1971) 345.
[135] R. Calì, S. Musumeci, C. Rigano, S. Sammartano, Inorg. Chim. Acta 56 (1981) L11.
[136] S. Capone, A. De Robertis, C. De Stefano, R. Scarcella, Talanta 32 (1985) 675.
[137] S. Capone, A. Casale, A. Currò, A. De Robertis, C. De Stefano, S. Sammartano, R. Scarcella, Ann. Chim. (Rome) 76 (1986) 441.
[138] A. Casale, A. De Robertis, F. Licastro, Thermochim. Acta 143 (1989) 289.
[139] P.G. Daniele, A. De Robertis, C. De Stefano, S. Sammartano, J. Sol. Chem. 18 (1989) 23.
[140] A. Casale, A. De Robertis, F. Licastro, C. Rigano, J. Chem. Res. 204 (1990) 1601.
[141] L. Abate, C. De Stefano, P. Mineo, J. Chem. Res. (1991) 76.
[142] L. Abate, R. Maggiore, C. Rigano, C. De Stefano, Talanta 38 (1991) 449.
[143] C. De Stefano, A. Gianguzza, S. Sammartano, Thermochim. Acta 214 (1993) 325.
[144] K. Sudhakar, M. Erecinska, J.M. Vanderkooi, Eur. J. Biochem. 230 (1995) 498.
[145] A. De Robertis, C. Foti, A. Gianguzza, C. Rigano, J. Sol. Chem. 25 (1996) 597.
[146] L.E. Kapinos, B. Song, H. Sigel, Inorg. Chim. Acta 280 (1998) 50.
[147] C. De Stefano, C. Foti, S. Sammartano, J. Chem. Eng. Data 44 (1999) 744.
[148] L.E. Kapinos, B. Song, H. Sigel, Chem. Eur. J. 5 (1999) 1794.
[149] L.E. Kapinos, H. Sigel, Inorg. Chim. Acta 337 (2002) 131.
[150] U. Bachrach, Functions of Naturally Occurring Polyamines, Academic Press, New York, London, 1973.
[151] U. Bachrack, Y.M. Heimer, The Physiology of Polyamines, CRC Press, Boca Raton, FL, 1989.

[152] D.R. Morris, L.J. Marton (Eds.), Polyammines in Biology and Medicine, Marcel Dekker, New York, 1981.
[153] R.M. Moision, P.B. Armentrout, J. Phys. Chem. 106 (2002) 10350.
[154] H. Schmidbaur, H.G. Classen, J. Helbig, Angewandte Chemie 29 (2003) 1090.
[155] S. Fox, I. Bushing, W. Barklage, H. Strasdeit, Inorg. Chem. 46 (2007) 818.
[156] C. Blaquiere, G. Berthon, Inorg. Chim. Acta 135 (1987) 179.
[157] I. Brandariz, F. Arce, X.L. Armesto, F. Penedo, M.E. Sastre de Vicentre, Monatshefte fur Chemie 124 (1993) 249.
[158] A. Casale, A. De Robertis, C. De Stefano, A. Gianguzza, Thermochim. Acta 140 (1989) 59.
[159] A. Casale, A. De Robertis, C. De Stefano, A. Gianguzza, G. Patanè, C. Rigano, S. Sammartano, Thermochim. Acta 255 (1995) 109.
[160] C.W. Davies, G.M. Waind, J. Chem. Soc. Dalton (1950) 301.
[161] A. De Robertis, C. De Stefano, A. Gianguzza, Thermochim. Acta 177 (1991) 39.
[162] C. De Stefano, A. Gianguzza, Ann. Chim. (Rome) 81 (1991) 119.
[163] C. De Stefano, C. Foti, A. Gianguzza, S. Sammartano, Chem. Spec. Bioavail. 7 (1995) 1.
[164] C. De Stefano, C. Foti, A. Gianguzza, S. Sammartano, Mar. Chem. 72 (2000) 61.
[165] S. Fiol, I. Brandariz, M.E. Sastre de Vicente, Talanta 42 (1995) 797.
[166] R.F. Lumb, A.E. Martell, J. Phys. Chem. 57 (1953) 690.
[167] M. Maeda, K. Okada, Y. Tsukamoto, K. Wakabayashi, K. Ito, J. Chem. Soc. Dalton Trans. (1990) 2337.
[168] F. Rey, J.M. Antelo, F. Arce, F.J. Penedo, Polyhedron 9 (1990) 665.
[169] G. Anderegg, Critical Survey of Stability Constants of EDTA Complexes. IUPAC Chemical Data Series. No. 14, Pergamon Press, Oxford, 1977.
[170] G. Anderegg, Pure Appl. Chem. 54 (1982) 2693.
[171] G. Anderegg, F. Arnaud-Neu, R. Delgado, J. Felcman, K. Popov, Pure Appl. Chem. 77 (2005) 1445.
[172] K. Popov, H. Wanner, Biogeochemistry of chelating agents, in: B. Nowack, J.M. Vanbriesen (Eds.), ACS Symposium series 910, Washington DC, 2005, p. 50.
[173] G. Schwarzenbach, E. Kampitsch, R. Steiner, Helv. Chim. Acta 28 (1945) 828.
[174] G. Schwarzenbach, H. Ackerman, Helv. Chim. Acta 30 (1947) 1798.
[175] J. Botts, A. Chashin, H.L. Young, Biochemistry 4 (1965) 1788.
[176] G. Anderegg, Helv. Chim. Acta 50 (1967) 2333.
[177] J.I. Watters, O.E. Schupp, J. Inorg. Nucl. Chem. 30 (1968) 3359.
[178] G. Anderegg, Z. Naturforsch. B 31 (1976) 786.
[179] A.R. Felmy, M.J. Mason, J. Sol. Chem. 32 (2003) 283.
[180] A.R. Fiorucci, L.R. de Paula, E.A. Neves, E.T.G. Cavalheiro, J. Chem. Eng. Data 47 (2002) 1510.
[181] E. Wanninen, (Ed.), Complexometric Titrations with Diethylenetriamino Penta-Acetic Acid, Acta Acad. Aboensias. Math. Et Phys. XXI, Abo Akademi, Abo., 1960.
[182] K. Kumar, P. Nigam, J. Phys. Chem. 84 (1980) 140.
[183] C. De Stefano, S. Sammartano, A. Gianguzza, D. Piazzese, Anal. Bioanal. Chem. 375 (2003) 956.
[184] F. Crea, C. De Stefano, A. Gianguzza, D. Piazzese, S. Sammartano, Chem. Spec. Bioavail. 15 (2003) 75.
[185] R.M. Smith, A.E. Martell, Y. Chen, Pure Appl. Chem. 63 (1991) 1015.
[186] J.M. Blair, Eur. J. Biochem. 13 (1970) 384.
[187] A. De Robertis, C. De Stefano, S. Sammartano, R. Calì, R. Purrello, C. Rigano, J. Chem. Res. 164 (1986) 1301.
[188] S.M. Shambhag, G.R. Choppin, Inorg. Chim. Acta 138 (1987) 187.
[189] F.J. Millero, Physical Chemistry of Natural Waters, Wiley-Intersciences, New York, 2001.
[190] C. De Stefano, C. Foti, A. Gianguzza, S. Sammartano, Chem. Spec. Bioavail. 10 (1998) 27.
[191] C. De Stefano, C. Foti, A. Gianguzza, D. Piazzese, S. Sammartano, in: A. Gianguzza, E. Pelizzetti, S. Sammartano (Eds.), Chemistry of Marine Waters and Sediments, Springer-Verlag, Berlin, 2002, p. 221.
[192] A. De Robertis, C. De Stefano, C. Foti, A. Gianguzza, D. Piazzese, S. Sammartano, J. Chem. Eng. Data 45 (2000) 996.
[193] C. De Stefano, C. Foti, A. Gianguzza, S. Sammartano, Analytica Chim. Acta 418 (2000) 43.
[194] P. Demianov, C. De Stefano, A. Gianguzza, S. Sammartano, Env. Tox. Chem. 14 (1995) 767.
[195] P.G. Daniele, M. Marangella, Ann. Chim. (Rome) 72 (1982) 25.
[196] P.G. Daniele, S. Sonego, M. Ronzani, M. Marangella, Ann. Chim. (Rome) 75 (1985) 245.
[197] P.G. Daniele, A. De Robertis, S. Sammartano, Ann. Chim. (Rome) 82 (1992) 503.
[198] P.G. Daniele, in: A. Braibanti, V. Carunchio (Eds.), I Complessi Metallici in Soluzione, Aracne Editrice, 1999, p. 475.
[199] E. Prenesti, P.G. Daniele, S. Toso, V. Zelano, S. Berto, Chem. Spec. Bioavail. 16 (2004) 17.
[200] A. Fini, G. Fazio, M. Gonzalez-Rodriguez, C. Cavallari, N. Passerini, L. Rodriguez, Inter. J. Pharmac. 187 (1999) 163.
[201] A. Schunk, A. Menert, G. Maurer, Fluid Phase Equilibr. 224 (2004) 55.
[202] D.N. Misra, Colloid Surface A 141 (1998) 173.
[203] H.S. Dunsmore, D. Midgley, J. Chem. Soc. (A) (1971) 3238.
[204] A. Tromans, G. Hefter, P.M. May, Aust. J. Chem. 58 (2005) 213.
[205] A. De Robertis, P. Di Giacomo, C. Foti, Anal. Chim. Acta 300 (1995) 45.
[206] P.G. Daniele, S. Berto, E. Prenesti, in ISMEC 2007 XVIII Italian-Spanish Congress on ”Thermodynamics of Metal Complexes, Cagliari (Italy), 2007, p. 18.
[207] A. Casale, A. De Robertis, S. Sammartano, Thermochim. Acta 95 (1985) 15.
[208] A. De Robertis, C. De Stefano, C. Rigano, S. Sammartano, R. Scarcella, J. Chem. Res. 42 (1985) 629.
[209] D.W. Archer, C.B. Monk, J. Chem. Soc. (1964) 3117.
[210] P.G. Daniele, A. De Robertis, C. De Stefano, S. Sammartano, Ann. Chim. (Rome) 80 (1990) 177.
[211] C. De Stefano, A. Gianguzza, D. Piazzese, J. Chem. Eng. Data 45 (2000) 15.
[212] C. De Stefano, A. Gianguzza, D. Piazzese, S. Sammartano, Analytica Chim. Acta 398 (1999) 103.
[213] A. Gianguzza, F. Maggio, S. Sammartano, Chem. Spec. Bioavail. 8 (1996) 17.
[214] C.W. Davies, J. Chem. Soc. (1938) 277.
[215] P.B. Davies, C.B. Monk, Trans. Faraday Soc. 50 (1954) 132.
[216] S.L. Dygert, G. Muzzii, H.A. Saroff, J. Phys. Chem. 74 (1970) 2016.
[217] K. Burger, P. Sipos, M. Veber, I. Horvath, B. Noszal, M. Low, Inorg. Chim. Acta 152 (1988) 233.
[218] H. Ren, B. Kratochvil, J. Chem. Eng. Data 40 (1995) 1091.
[219] P.G. Daniele, C. Rigano, S. Sammartano, Thermochim. Acta 62 (1983) 101.
[220] A. De Robertis, C. De Stefano, C. Rigano, S. Sammartano, Thermochim. Acta 202 (1992) 133.
[221] G.H. Nancollas, G.L. Gardner, J. Crystal. Growth 21 (1974) 267.
[222] B. Finlayson, A. Smith, L. Dubois, Invest. Urol. 13 (1975) 20.
[223] T. Hirokawa, Y. Kiso, J. Chromatography 248 (1982) 341.
[224] A. Casale, A. De Robertis, F. Licastro, Ann. Chim. (Rome) 82 (1992) 13.
[225] M. Walser, J. Phys. Chem. 65 (1961) 159.