

# Nature and Properties of Metal Cations in Aqueous Solutions

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## Abstract

Chemical nature, thermodynamic and kinetic properties of metal cations in aqueous solutions are described and discussed in terms of structural factors controlling physical properties of the systems. The structure of hydrated cations, reaction mechanism of water exchange on the cations, hydrolytic phenomena and acidity of the cations are presented. Correlations between coordination states of the salts in and bulk properties of the solutions are indicated. Elements of aquatic chemistry are presented.

**Keywords:** solutions, ionization, cations, solutions structure, hydration, water exchange, hydrolysis, acidity, sea water.

The commonest and most important solvent, water, is one of the most interesting since in aqueous solutions of salts interactions between ions and solvent molecules profoundly affect interactions between the ions as well as between the solvent molecules.

Current ideas of ions in aqueous solutions consist of models that are consistent with electrostatic interactions between the ions and polar water molecules and their effects on the localized structures of liquid water in the immediate vicinity of the ions. The smallest number of immediate neighbours around a naked ion is known as the coordination number, a number that may have values from 4 to 12 for cations, depending on ion size and electronic nature. However, the majority of metal ions, particularly those of d-block elements, have a primary hydration number of six.

A paper of Pasquarello and co-workers published in 2001 in *Science*, describes a diverse adoption on the part of researchers investigating properties of aqueous solutions of simple electrolytes – from enthusiasm to cool reserve. Results of the research as well as experiments and calculations presented in this paper show us that copper (II) ions in aqueous solutions of salts of coordinatively inactive anions occur

in the form of hydrates containing five water molecules, i.e. hydrated cations of a form of  $\text{Cu}(\text{H}_2\text{O})_5^{2+}$  [1, 2].

It has been commonly accepted until now that  $\text{Cu}^{2+}$  ions as well as many other cations of the third period,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ , exist in water in an octahedral surrounding of six oxygen atoms derived from six molecules of water, which are included in a the  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  – hydrated cation. A fact that the properties of this hydrate differ from properties, that can be observed in the case of other cations of the  $\text{M}(\text{H}_2\text{O})_6^{2+}$  type, was usually explained in terms of a deformation of the octahedral symmetry being the results of Jahn–Teller's effect.

A hydrated  $\text{Cu}(\text{H}_2\text{O})_5^{2+}$  cation, whose existence is postulated by Pasquarello and co-workers, is a dynamic structure, whose existence can be described as a series of equilibrium states between complexes of a tetragonal pyramid structure and complexes of a structure of trigonal bipyramid.

A more complicated situation was observed in the case of trivalent lanthanides. Recently obtained results of research on neutron diffraction confirms the prior observations that a coordination number decreases from nine to eight as an atomic number of the lanthanides series increases [3]. However, a value of 8.5 observed for coordination number of the  $\text{Sm}^{3+}$  cation is explained in terms

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of equilibrium between hydrates of the mentioned above coordination numbers, i.e.:



The situation of a hydrated  $\text{Be}^{2+}$  cation is definitely more simple and unambiguous. An indisputable fact is that it exists exclusively in the form of a one and only hydrate of the co-ordination number of 4, in other words as the complex ion,  $\text{Be}(\text{H}_2\text{O})_4^{2+}$ . It is an obvious consequence of the electron structure of  $\text{Be}^{2+}$  cation [4, 5].

The four water molecules are expected to be tetrahedrally arranged around the central  $\text{Be}^{2+}$  ion, both from a ligand-ligand repulsion and also if the acceptor orbitals for the coordination bonds are the 2s and three 2p atomic orbitals.

Water molecules that are the nearest neighbours of metal cation form the primary hydration sphere. An existence of so-called secondary hydration sphere (sometimes called a second hydration shell) is a typical phenomenon in the case of aqueous solutions of electrolytes. A secondary hydration sphere consists of water molecules that are hydrogen-bonded to those in the primary hydration shell. A formation of the secondary hydration sphere is a consequence of the fact that protons of water molecules directly bonded to hydrated cations are of more acidic nature and they can form relatively strong hydrogen bonds. The secondary hydration sphere of an octahedral cation, which is hydrated directly with six molecules of water, consists of six or even twelve consecutive water molecules. After all each molecule of water, which is included in the first shell, has the two protons. This means that the  $\text{M}(\text{H}_2\text{O})_6^{n+}$  cation can be presented by means of formula  $\text{M}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_6^{n+}$  or even  $\text{M}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{12}^{n+}$ . The molecules of the secondary hydration sphere experience some electrostatic forces from the central metal ion. Thus, their properties depend on its nature.

Equilibria, which are established in solutions, are of dynamic nature and chemical individuals occurring in the system, which from the thermodynamical point of view remain in equilibrium state, undergo continuous changes, they are either forming or disintegrating. In some cases, the water molecules, which can enter and leave the coordination sphere of hydrated cations millions and even billions of times every second, undergo exchange with unbounded water molecules from the nearest surrounding of hydrate, i.e. the molecules forming the "bulk" solvent. Such a situation takes place in the case of the  $\text{Cu}^{2+}$  and  $\text{Gd}^{3+}$  ions. The opposite situation sometimes takes place and a time of residence of water molecule in the primary hydration sphere of an ion happens to be very long, exceeding a million seconds in the case of the  $\text{Cr}^{3+}$  ion. However, it is proper to add that hydration sphere of the  $\text{Ni}^{2+}$  cation is considered as a long-lived one in view of the fact that the stay time of water molecules in direct environment of this cation is of 10 microseconds [6].

It should be noted that the properties of water are significantly changed by the application of high pressure, variation of temperature, and the dissolution of salts. The results of structural investigation performed at 573 K and 100 MPa show that the hydration structure is completely destroyed under these extreme conditions, and suggest that the structure is completely dominated by cation-anion interactions [7].

The simple process, known as a solvent-exchange reaction due to its symmetry, is regarded as being one of the most fundamental reactions. The mechanism of such exchange of water molecules, its stages and intermediate products are the facts, which are not identified and established finally. We don't even know it in regard to the most common octahedral structures. The rate constants of exchange of water molecules are the only known data. And we don't know whether the mechanism of the process of water molecule exchange is either a dissociative (**D**) or an associative (**A**) one. In the case of mechanism of the **D** type, the exchange of water molecules is a two-stage process. The first stage consists in removal of water molecules and it results in the formation of more or less stable transient complex



The second stage consists of the addition of water molecule and reconstruction of initial hydrate



The water molecules exchange process can also run in the associative way (**A**). The water molecule addition to hydrate and formation of intermediate individual of coordination number 7 is the first stage in this case, in other words the process:



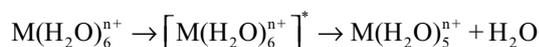
is connected with process of reconstruction of the primary structure:



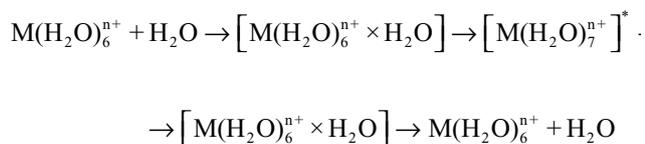
with another water molecule included in its composition.

Both mechanisms mentioned-above, the dissociative and associative one, are characteristic for extreme cases. In order to consider that the exchange process of water molecule runs according to one of them, the intermediate product, in this case  $\text{M}(\text{H}_2\text{O})_5^{n+}$  or  $\text{M}(\text{H}_2\text{O})_7^{n+}$ , must be stable enough to be detected. In view of the fact that it isn't always possible, an intermediate interchange (**I**) mechanism is considered. The opinion of some investigators is that there are more options to choose from than these three mechanisms according to the phrase "the more the better". So we can distinguish a dissociative interchange mechanism ( $\text{I}_d$ ) and an associative interchange one ( $\text{I}_a$ ).

Different mechanisms of attacking the hydrated ion with water molecules are also considered. After all, the formation of intermediate products corresponding to the **D** or **A** mechanisms is not a simple process. The hydrate molecule must undergo excitation and relaxation and that is when the splitting off molecule of water can take place. It occurs according to the simplified scheme:



The first stage consists in binding of the water molecule by cation in the case of associative mechanism. The resultant aggregate transforms into an intermediate product, which undergoes further disintegration.



However, when making a full description of the above processes, we should take into account the changes, which occur inside the secondary hydration sphere and this description becomes very complicated in this way.

When answering the above questions we should determine entropy and volume of activation of water molecule exchanges and it amounts to investigation of the influence of both the temperature and pressure on the NMR spectrum. It is not necessary to add that investigating the influence of high pressure on the NMR is not simple and a very specialized instrumentation is required.

An analysis of solvent molecule exchange makes a great opportunity to display a talent of creators and users of computational method, in which the latest achievements of molecular dynamics and/or quantum chemistry are employed and successful attempts of attribution of water-exchange mechanisms of transition-metal

hexaaqua ions using quantum chemical methods are described [8, 9].

It is intuitively obvious that chemical reactivity of the  $M(H_2O)_6^{n+}$  hydrates is connected with reactivity of the intermediate products of formula  $M(H_2O)_5^{n+}$ , which forms during water molecules exchange.

A diversification of lability, in other words susceptibility of hydrated cations to exchange of water molecules, finds its reflection in the stability of forming complexes, diversification of thermodynamic, kinetics and hydrodynamic properties of hydrated cations as well as in the rate of electrode processes. This situation becomes much more complicated when ligand exchanges should be considered, especially ligands that can form chelate complexes. There are many questions which can be answered only today since the NMR spectrophotometers of frequency exceeding 500 MHz are generally available.

There was a general opinion until quite lately that properties of strong electrolytes are determined with the fact that they are entirely dissociated. Various models of solutions were formulated and described when considering many effects and phenomena. There were considered both the hydrolysis and formation of complexes of various types. The models describing chemical properties were created in this way. The influence of any types of ions on solvent structure, in this case on water, were analyzed. We can't mention all the techniques which were employed for the aqueous solution research.

Along with genesis and development of the new research methods and especially along with progress in computer techniques we realized that even in the case of water solutions of the simplest salts the real terms deviate considerably from the seemingly unambiguous and clear picture that was created, beginning from the times of Arrhenius (1887). And it is this picture that is fixed in many handbooks of chemistry, especially general chemistry.

Table 1. Ionization of salts in aqueous solutions at 25°C [10, 11].

Salt	Ionic Strength (M)	Fraction of Metal Present as Each Species			
		Species	Fraction	Species	Fraction
KCl	0.5	K <sup>+</sup>	0.95	KCl	0.05
CsCl	0.5	Cs <sup>+</sup>	0.90	CsCl	0.10
Na <sub>2</sub> SO <sub>4</sub>	0.5	Na <sup>+</sup>	0.76	NaSO <sub>4</sub> <sup>-</sup>	0.24
K <sub>2</sub> SO <sub>4</sub>	0.5	K <sup>+</sup>	0.70	KSO <sub>4</sub> <sup>-</sup>	0.30
MgSO <sub>4</sub>	0.1	Mg <sup>2+</sup>	0.58	MgSO <sub>4</sub>	0.42
MgCl <sub>2</sub>	1.0	Mg <sup>2+</sup>	0.70	MgCl <sup>+</sup>	0.30
CaCl <sub>2</sub>	1.0	Ca <sup>2+</sup>	0.70	CaCl <sup>+</sup>	0.30
BaCl <sub>2</sub>	1.0	Ba <sup>2+</sup>	0.80	BaCl <sup>+</sup>	0.20
CuCl <sub>2</sub>	1.0	Cu <sup>2+</sup>	0.70	CuCl <sup>+</sup>	0.30
CuSO <sub>4</sub>	0.1	Cu <sup>2+</sup>	0.56	CuSO <sub>4</sub>	0.44
CdCl <sub>2</sub>	1.0	Cd <sup>2+</sup>	0.01	CdCl <sup>+</sup>	0.31

Firstly, we should ask a simple question: Does the expression that the salt is entirely dissociated means that it is entirely ionized? After all, every electrolyte undergoes association to some degree and complex compounds of different types are formed in most cases.

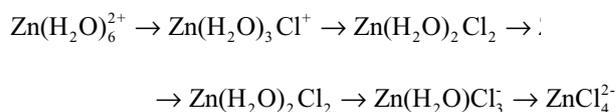
It is not necessary to make complicated experimental measurements. It is enough to compare the colour of concentrated aqueous solutions of  $\text{Fe}(\text{ClO}_4)_3$  acidified with  $\text{HClO}_4$  with the colour of the  $\text{FeCl}_3$  solution. The first of them is of a violet-pink colour typical for the hydrated  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  cations and the second one is of an intensive yellow-orange colour generally considered as typical for the iron (III) salt solutions. The addition of a small quantity of hydrochloric acid to the first  $\text{Fe}(\text{ClO}_4)_3$  solution is enough to obtain the colour expected for the iron (III) and it is not necessary to add that this colour is typical for chloride complexes of the  $\text{Fe}^{3+}$  ions. A simple experiment consisting in dilution of the  $\text{Fe}(\text{ClO}_4)_3$  solution is also convincing. The change of colour is connected with the hydrolysis phenomenon and consequently with the formation of iron (III) hydroxy-complexes[10].

The author of the above description of the iron (III) salt properties tries to fight against convictions resulting from accepted opinion established in handbooks. He described, in the popular *Journal of Chemical Education*, the results of calculations based on stability constants published by Martell in 1993 [11]. Some of them are presented in Table 1. A detailed analysis is not necessary to realize that the aqueous solutions of simple salts can hardly ever be discussed as entirely ionized. So everybody should be aware of the fact that it is not as easy as it was considered until now, how to answer the question about concentration of the  $\text{Cu}^{2+}$  ions in a 0.045 M solution of  $\text{CuSO}_4$ . Similarly, the  $\text{La}^{3+}$  ions concentration in a 0.40 M solution of  $\text{LaBr}^{2+}$  does not amount to 0.40 M at all, and at least a third of the La is present as  $\text{LaBr}^{2+}$  [10]. Everybody should take into consideration the result of measurement carried out by means of the ion-selective electrode. It also concerns solutions of other salts.

The following simple question is how can we explain differences in properties of aqueous solutions of such simple salts as  $\text{CaCl}_2$  and  $\text{ZnCl}_2$  or  $\text{CaBr}_2$  and  $\text{ZnBr}_2$ ? Their activity coefficients are different and they change together with the salt concentration in different ways. Why do such solutions vary also with compressibility and thermal expansibility? It is easy to answer the question why the speed of ultrasounds propagation is higher in aqueous solutions of  $\text{CaCl}_2$  and  $\text{CaBr}_2$  than in pure water. But why is the speed of sound propagation lower in aqueous solutions of  $\text{ZnCl}_2$  and  $\text{ZnBr}_2$  than in pure water? [12].

These questions were answered not long ago – in the year 1995. The nature and structure of complexes, which are formed in such solution were unambiguously determined on the basis of analysis of Raman's spectra and the research of X-rays diffraction in concentrated solutions of  $\text{ZnCl}_2$  and  $\text{ZnBr}_2$  [13]. It was also determined that the zinc (II) ions occur in the form of octahedral hydrated

cations of formula  $\text{Zn}(\text{H}_2\text{O})_6^{2+}$  only in the case of solutions of these salts near a dilution limit. More and more complicated tetrahedral chloride complexes form along with increase of concentration:



Furthermore, complicated polymeric forms arise in the case of the most concentrated solutions. Following resultant coordinative forms of zinc chloride interact with water in different ways and influence its structure in their nearest and farther surrounding variously. It means that properties of solutions must be different and it should not amaze us that the average ionic activity coefficients of zinc chloride in water considerably differ from typical values of calcium chloride. Diversity of speed of sonic waves propagation results from the fact that the speed of sound waves propagation is higher when the medium elasticity is greater. The aqueous solution of  $\text{CaCl}_2$  or  $\text{CaBr}_2$  is a medium which is more elastic than water. Its structure is more ordered than the structure of pure water. It happens in the case of free hydrated  $\text{Ca}^{2+}$  cations and corresponding anions, which can also hydrolyze. These interactions are of electric nature and they dominate local structure dislocations connected with the formation of hydration zone. There is no such interaction in the case of the  $\text{ZnCl}_2$  and  $\text{ZnBr}_2$  solutions where the  $\text{Zn}^{2+}$  ions occur in the form of electrically inactive dihalide complexes and electrically inactive polymeric structures, which decrease medium elasticity when disturbing the structure of water, thus decreasing the speed of sound propagation.

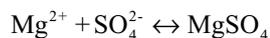
It is obvious that in the case of each attempt of explaining and interpreting physical properties of solutions, both these occurring in laboratories as well as in nature and industry like sea water, body fluids or any other electrolyte solutions the knowledge of coordination states of salt in solutions, i.e. full information about hydrates, ion pairs and complex compounds, is required. It is connected, among other things, with medical diagnostic methods relied on tissues display, i.e. by means of methods in which resonance phenomena and ultrasounds are used.

We can meet similar phenomena, i.e. consecutive chloride complex formation, in the case of solutions, in which mercury (II) and lead (II) are present. Mercury (II) and lead (II) exist in different forms and proportions depending on the ratio of chloride ion, concentration to total concentration of metal. For example, in the case when concentration of chloride ions is about 0.15 M, this value corresponds to both the physiological conditions and composition of sea water, the amount of 45% of mercury (II) occurs as the  $\text{HgCl}_4^{2-}$  anionic complex, 30% as the  $\text{HgCl}_3^-$  complex anion and 25% in a form of electrically neutral  $\text{HgCl}_2^0$  complex.  $\text{PbCl}^+$ , that is to say monochloride complex, is a dominant complex of lead (II) in the same conditions. The forms in which these metals occur are determined by pH of solution in the case of natural

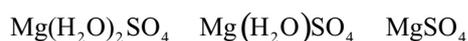
waters and body fluids, in other words in real conditions. The number of complexes which can coexist successively increases considerably in the case of such systems. For example as many as seven different complex compounds of lead (II) can be formed in such a considerably simple system as  $\text{Pb}^{2+}$  -  $\text{Cl}^-$  - cysteine [14]. The knowledge of forms in which these toxic metals occur is of a basic meaning in the case of selection of extractive agents used for therapy for metals poisoning, water purification and soil remediation.

Thus, it isn't enough to employ the classic chemical analysis. A speciation analysis is required. It is a very serious problem in the case of environmental analytics. There are numerous naturally occurring organic ligands (apart from simple anions), which occur in samples of natural waters containing heavy metal ions. The complexes differ with thermodynamic and kinetic stability. The use of complicated procedures is required for determination of "free" metal ions. Some of these procedures consist of the use of ligands exchange. Xue and Sigg proposed a method of determination of  $\text{Cd}^{2+}$  ions in natural waters consisting in titration of the sample solution with solution containing  $\text{Cd}^{2+}$  in the presence of ethylenediamine [15]. The described method is a convincing illustration of the fact that knowledge about the basic properties of complex compounds, both thermodynamic and kinetic, is necessary to elaborate the correct analytical method of determination of metal ions, especially in the case of such low levels of concentration as in the case of  $\text{Cd}^{2+}$  content in natural waters.

We deal with very complicated phenomena in the case of such simple systems like solutions of salts consisting of ions commonly considered as completely devoid of coordinative properties. The research on  $\text{MgSO}_4$  solutions by means of classic electrochemical methods allow us to state only this fact that the association phenomena occurs in the system:



Only the detailed research of ultrasound absorption carried out by Eigen and Tamm has resulted in the determination that three types of ion pairs coexist in aqueous solutions of  $\text{MgSO}_4$  in equilibrium state, namely:

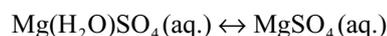
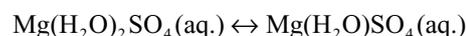
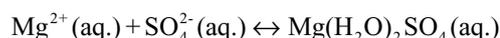


These ion pairs differ between themselves with the number of water molecules between cation and anion [16]. The first ion pair arises as a result of the simple association of the two hydrated ions and the last one, the so-called contact ion pair. Without going into details of the structure of these ion pairs, which are the subject of investigations and disputes, we should take into consideration that each of these forms is hydrated. Furthermore, the phenomena of both exchange of water molecules and exchange of sulphate ions occur in all the systems.

In conclusion,  $\text{MgSO}_4$  in aqueous solution exists in four different forms and measurements carried out on the basis of equilibrium methods, i.e. conductometric and potentiometric measurements, making it possible to determine the total association constant, which is defined as:

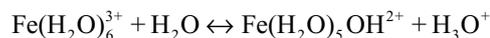
$$K_{\text{as}} = \frac{[\text{Mg}(\text{H}_2\text{O})_2\text{SO}_4] + [\text{Mg}(\text{H}_2\text{O})\text{SO}_4] + [\text{MgSO}_4]}{[\text{Mg}^{2+}] \times [\text{SO}_4^{2-}]}$$

In order to obtain the full description of the  $\text{MgSO}_4$  system properties, the three equilibria should be taken into account. We can present them in the simplified way by means of the following equations

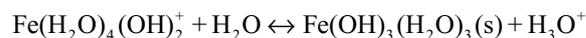
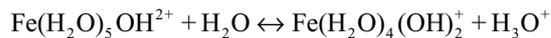


The same ion pairs are formed in sea water and we can evaluate that about 10% of magnesium, which it contains, occurs exactly in this form [17]. So we should ask the question concerning interpretation of indications of ion-selective electrodes once again.

The issue is more complicated in the case of solutions of the transition metals salts. This fact is exemplified by means of the above-mentioned solutions of  $\text{FeCl}_3$ . It was shown that in the case of 0.1 M solution of this salt only 10% of iron (III) exists as the  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  hydrated ions. As regards the remainder, 42% occurs as  $\text{FeCl}(\text{H}_2\text{O})_5^{2+}$ , 40% as  $\text{FeCl}_2(\text{H}_2\text{O})_4^+$ , 6% as  $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$  and 2% in the form of  $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$  [10]. This means that the hydrated  $\text{Fe}^{3+}$  cations hydrolyze simultaneously with formation of the chloride complexes of iron (III):



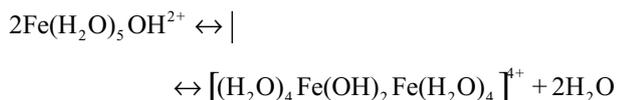
Hydrogen ions are released as a result of hydrolysis and, consequently, solutions containing the  $\text{Fe}^{3+}$  ions become acidic. Hydrolysis is a multistage process in the discussed case and formation of the consecutive hydroxy-complexes of iron (III) is described in terms of the system of equilibria:



The penultimate of these equilibria, leads up to the formation of electrically inactive individuals presented with formula  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$ , which is stable in solid

phase. Only in the case of the  $\text{Fe}^{3+}$  cations does hydrolysis proceed so far, i.e. in such a degree that the formation of anionic complexes occurs and their structure can be described as  $\text{Fe}(\text{OH})_4(\text{H}_2\text{O})_2^-$  [18].

Further reactions of hydrolysis products, which result in the formation of the two and multinuclear complexes, sometimes called isopolycations, are the next stages of the process. In the case of hydrolysis of the  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  cation, dimerization takes place as a result of condensation reaction resulting in the formation of the two hydroxide bridges:

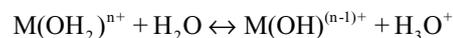


The resultant dimer may undergo additional hydrolytic reactions accompanied by the formation of more  $-\text{OH}$ - and  $-\text{O}-$  bridges as well as larger and larger molecules. It was also proved that the same multinuclear complexes arise during dissolution of solid phases of different types and that they can exist for years in a form of metastable phases [18].

The simplified scheme presented above is not limited only to the salts of iron (III). Metals cations of a charge number  $z = +1$  are also hydrated with water molecules. The same phenomenon takes place in the case of metals ions of the charge number  $z = +2$  in the pH range from 6 to 12. Trivalent cations occur in a form of hydroxo metal complexes in the range of pH values typical for natural waters. In the case of charge number  $z = +4$  hydrates are too acidic to form solutions exhibiting properties typical for natural water systems. The  $\text{Th}^{4+}$  ion is the one of very few exceptions. However, the solubility of Th(IV) in neutral pH is dominated by the formation of colloidal systems.

Acidity of metals cations is a common phenomenon. It is worth not only remembering that solutions of iron (III) salts can be more acidic than solutions in which  $\text{Al}^{3+}$  ions occur, but also realizing that in both these cases solutions can be as acidic as solutions of acetic acid. The  $\text{pK}_a$  value for acetic acid amounts to 5.0.

The  $\text{pK}_a$  values are considered a measure of acidity of the hydrated cations. These values correspond to hydrolysis reaction, which can be described by means of the equation:

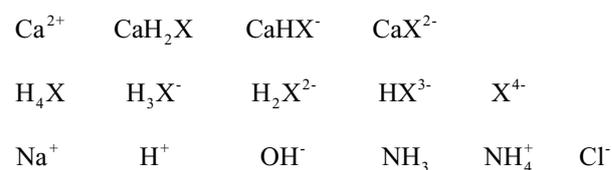


which is simplified by the use of only one molecule of water.

In Table 2 the  $\text{pK}_a$  values for chosen metals cations calculated by Hawkes based on stability constants of adequate hydroxy-complexes are presented [19]. The presented data shows, among other things, that in the case of metals of the 1, 2 and 3 groups, cation acidity decreases as the atomic number of cation increases. It can also be seen that acidity increases together with increase of the charge number of ion.

One can accept that the presence of each cation, even such as  $\text{K}^+$ , can change the pH value of solution in second place after decimal point and in the case of the  $\text{Li}^+$  ions and alkaline earth metals such as  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , even in the first place. It is applied to such systems in whose other acids, whose presence can blur the dissociation effects of other hydrates, do not exist.

The well known  $\text{Ca}^{2+}$ -EDTA system already met by each chemist when determining the total hardness of water by means of sodium versenate illustrates complexity of equilibria established in solutions containing polydentate polyfunctional ligands. A dozen or so various molecules, ions and complex combinations can be present simultaneously in this system. These are the most important of them:



The  $\text{X}^{4-}$  symbol stands for the EDTA anion. The least stable individuals such as the  $\text{Na}^+$ -EDTA complexes

Table 2. The  $\text{pK}_a$  values of hydrated cations at 25°C [19].

Ionic Strength (M) = 0					
$\text{Li}^+ = 13.6$	$\text{Be}^{2+} = 5.4$				
$\text{Na}^+ = 13.9$	$\text{Mg}^{2+} = 11.2$				$\text{Al}^{3+} = 5.0$
$\text{K}^+ = 14.0$	$\text{Ca}^{2+} = 12.7$	$\text{Sc}^{3+} = 4.3$		$\text{Zn}^{2+} = 9.0$	$\text{Ga}^{3+} = 2.6$
	$\text{Sr}^{2+} = 13.2$	$\text{Y}^{3+} = 7.7$	$\text{Zr}^{4+} = -0.3$	$\text{Cd}^{2+} = 10.1$	$\text{In}^{3+} = 3.9$
	$\text{Ba}^{2+} = 13.4$	$\text{La}^{3+} = 8.5$	$\text{Hf}^{4+} = 3.4$	$\text{Hg}^{2+} = 3.4$	$\text{Tl}^{3+} = 0.6$
Transition metals of the 3d <sup>n</sup> series					
	$\text{V}^{3+} = 2.3$	$\text{Cr}^{3+} = 3.7$	$\text{Mn}^{3+} = -0.6$	$\text{Fe}^{3+} = 2.2$	$\text{Co}^{3+} = 0.5$
	$\text{V}^{2+} = 6.5$	$\text{Cr}^{2+} = 5.5$	$\text{Mn}^{2+} = 10.6$	$\text{Fe}^{2+} = 9.4$	$\text{Co}^{2+} = 9.7$

and ion pairs formed by the  $\text{Ca}^{2+}$  cation and mother anion were overlooked to simplify the scheme. The equilibrium state is determined by means of the pH of solution and the stability of calcium complexes, which arise in system. The problem becomes much more complicated in the case of simultaneous occurrence of the calcium and magnesium ions.

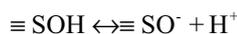
We should take into consideration the interactions between ions and surface of particles of different origin suspended in water when analyzing ion equilibria established in natural waters. The particles of inorganic origin are different oxides (they are  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  among other things), carbonates (for example  $\text{CaCO}_3$ ), sulphides and silty minerals.

The organic particles are, first of all, a matter of biological origin, dead debris of animals and plant and products of their decomposition. Live organisms such as bacteria and algae also fulfill their role, sometimes rather importantly, in metal ions complexing. The size of molecules and, consequently, the dimensions of active surface of these molecules fulfill a role of the essential factor. Transition of molecule sizes in the range characteristic for colloids is accompanied by a fundamental change of properties.

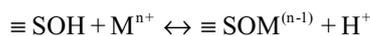
Different functional groups such as  $-\text{OH}$ ,  $-\text{CO}_3\text{H}$ ,  $-\text{SH}$ ,  $-\text{COOH}$  and  $-\text{NH}_2$ , which may act as ligands for metal ions, occur on the surface of all particles. A number of such groups per unit of surface is characteristic of the given dispersed phase and together with its specific surface, as well as concentration, decides on properties of the system. These, which are present on the surface of oxides of the  $-\text{OH}$  group, take place in acid-basic equilibria and can be described by means of the equations:



and



where  $\equiv \text{SOH}$  presents the  $-\text{OH}$  group, which is situated on the surface of the dispersed phase. These can be the  $-\text{OH}$  groups bonded to atoms of both the metalloids and metals. The  $-\text{OH}$  groups are also employed in coordinative interactions with metal ions and usually these equilibria interfere with each other. Such cases can be described using the equation:



It is easy to notice that this equation describes the process occurring on the surface of an ion exchanger. Equilibria of this type are described by means of adequate complexing constants known as the surface complexing constants and represented with symbol  $K_s$ . The particle surfaces act as polyelectrolytes and a surface charge is built up, depending on pH and on the metal bound. The pH of natural waters, between 7.0 and 8.5, favours binding of metal ions to hydrous oxides. Amorphous oxides,

like  $\text{Fe}(\text{OH})_3(\text{s})$  and  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3(\text{s})$  have high surface and thus high capacities for binding of metal ions.

The surface of organic and biological particles contain various functional groups with different stability constants. Strong binding, e.g. of copper(II) on algae surfaces, have been observed, indicating that binding to biological surface is an important factor controlling the speciation of metal ions in natural waters [20].

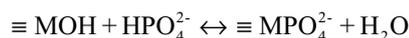
In the presence of coordinatively active anions in the system, the phenomenon on the surface of dispersed phase can be discussed as a process of ligands exchange, which results in release of the  $\text{OH}^-$  ions.



The  $\equiv \text{MOH}$  symbol stands for the  $-\text{OH}$  group linked to the atom of metal. A surface deprotonation of ligands (i.e. that which occurs on the surface of dispersed phase) can also take place



and even



The above phenomena are greatly responsible for vertical transport of metals in natural water reservoirs, especially in water of seas and oceans. Consequently they are responsible for the formation, composition and morphology of bottoms, herein so-called iron-manganese concretions and clusters of useful minerals.

Interactions at the solid phase surface-solution interface recently became a subject of interest of both the scientific journals such as *Science* and the daily press, i.e. the Polish *Gazeta Wyborcza* dated April 23, 2004, which described results of an experiment consisting of "fertilizing" the South Seas with comminuted metallic iron, which is known as SOFeX – *Southern Ocean Iron Experiment*. The aim of the SOFeX project was to check a hypothesis assuming that phytoplankton, which absorb carbon dioxide from the atmosphere when feeding iron contained in dust blown from the steppes of Asia, are responsible for decreasing Earth's temperature in the past. The so-called "iron hypothesis" holds that by adding small amounts of iron, an essential micronutrient, to ocean waters rich in other nutrients, aquatic plants can be made to bloom vigorously, thus removing enough carbon dioxide from the atmosphere to offset the greenhouse effect. It has been shown that for every atom of iron added to the water, the plankton carried between 10,000 and 100,000 atoms of fixed carbon below 100 meters upon sinking. Each of these process stages is connected with the above-mentioned properties of hydrated metals cations, in particular with properties of the  $\text{Fe}^{3+}$  cation. Attempts of formulating a mathematical model describing these important processes requires in-deep knowledge of inorganic chemistry, coordination chemistry and thermodynamics of solutions.

Sea water is the largest and most important natural ionic environment. Ocean waters cover about 71% of the globe and its volume is estimated at about 1,350 million km<sup>3</sup>, which makes 97% of water resources of our globe. The water itself is made up of more than 96% sea water. For it is generally accepted that salinity of ocean waters amounts to about 3.5%. It is a little lower in Polar Regions and a little higher in equatorial regions. The low salinity is characteristic for cold semi-closed seas. The Baltic Sea is such a reservoir, in which salinity depends on depth and fluctuates between 0.8 to 1.8%. Semi-closed tropical seas are characterized with high salinity – reaching 4.5% in the case of the Red Sea. We should clearly emphasize that such ions as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, being the so-called group of basic sea salt components, make up more than 99% of a mass of inorganic salts dissolved in sea water. Their relative mass ratios are approximately constant and observed oscillations are connected with local (on an ocean scale) biological, hydrological and geochemical processes [21].

The total content of calcium and magnesium in sea water, according to its elaborated models, is determined by means of equations of the type below and considering formation of the three basic associated molecules:

$$(\text{M}^{2+})_{\text{tot}} = [\text{M}^{2+}] + [\text{MSO}_4^0] + [\text{MHCO}_3^+] + [\text{MCO}_3^0]$$

where M<sup>2+</sup> stands for the Ca<sup>2+</sup> or Mg<sup>2+</sup> ions. It gets out of accessible data that *ca.* 91% of Ca<sup>2+</sup> ions present in sea water occur in a form of free ions and participation of consecutive ion pairs adequately amount to 8.0, 1.0 and 0.2%. In the case of Mg<sup>2+</sup> ions the participation of free ions is lower and amounts to 87% and participation of ion pairs adequately amounts to 11.0, 1.0 and 0.3% [22].

Ions belonging to the above-mentioned group of elements determine the basic physicochemical properties of sea water. Cations of trace elements occur in much lower concentrations, i.e. in micro and submicrogramme quantities per 1 kilogram of sea water. These are such ions as Fe<sup>3+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Cu<sup>2+</sup>. They are of principle importance in the case of the whole biological processes series occurring in the sea environment. Being components of many enzymes in sea organisms, they significantly influence properties of the environment. Sea water is a main source of these elements occurring on the ocean bottom in a form of above-mentioned concretions, though their content in sea water is very low. The ocean waters fulfill a role of *mediator* in transport of mineral substances, which land in water as a result of decomposition, erosion, decay, oxidation and finally dissolution of rocks of different origin.

In view of the fact that concentrations of trace elements in sea waters are many times lower than concentrations of ions belonging to the basic group and organic substances of organic complex-forming properties, we should realise that adequate cations do not occur in the form of simple hydrates. In the case of North Pacific

waters it has been determined (among other things) that 70% of dissolved cadmium occurs in the form of complexes with organic ligands, which exist only in surface waters. Otherwise it is known that total concentration of cadmium in sea water depends on the distance from surface of water and increases with depth. This resulted in the fact that concentration of the free Cd<sup>2+</sup> ions in surface waters is of 20 fM, i.e. 20·10<sup>-15</sup> mol·dm<sup>-3</sup> while their concentration in abyssal waters is 1,000 times higher and amounts to 20 pM, i.e. 20·10<sup>-12</sup> mol·dm<sup>-3</sup>. The concentration of inorganic zinc, that is to say of the free Zn<sup>2+</sup> ions, changes in the same way. The value of this concentration is of about 2 pM, i.e. 2·10<sup>-12</sup> mol·dm<sup>-3</sup> in ocean surface waters and its order of magnitude increases with depths reaching 2 nM [23]. It is a fact of essential importance for all organisms living in the sea. After all there is no doubt about cadmium toxicity while zinc is necessary for life.

The above-mentioned example shows that concentrations of trace elements change with time and distance. It is the result of the fact that organic ligands concentration is a function of climatic conditions since it depends on seasons and geographical position.

The influence of gases dissolved in natural waters on the ionic equilibria were not considered in the above-mentioned remarks. Many other phenomena were even not mentioned. Among other things we did not make mention on many important phenomena connected with the processes of oxidation and reduction which occur in waters, and especially about the process of oxidation of sulphuretted hydrogen fundamental for organisms living in natural waters.

The author's intention was only to signal that there are some phenomena and problems which can take place in the everyday practice of the chemical engineer working on problems connected with protection of water environments. An opportunity to meet such problems during studies or in popular manuals is not too obvious. Chemistry of natural waters, well known under the English name *Aquatic Chemistry*, is new and all the time being developed. This very important part of environmental chemistry has been the subject of many serious studies, including manuals and sets of cases. The above-quoted book of Stumm and Morgan, as well as the handbook of Millero and also books of Morel and Hering, plus Pankow are worth recommending [24, 25].

Unfortunately, there is a lack of studies considering this important subject in Polish literature. Moreover, it is often passed over and neglected in programmes of studies of chemistry and environment protection.

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