Main Group Metal Chemistry *Vol. 23, No.8, 2000*

THE EFFECT OF SURFACE ACTIVE SUBSTANCES ON HYDROLYSIS OF ALUMINIUM(III) ION

Predrag Djurdjevic*, Ratomir Jelic and Dragana Dzajevic

Faculty of Science, Institute of Chemistry, p.o.box 60, 34000 Kragujevac, Yugoslavia
<preza@ptt.yu> fax: 381 34 335 040

ABSTRACT

The hydrolysis of aluminium(III) ion has been studied in 0.01, 0.1 and 1.0 mol/L LiCl ionic medium, at 298 K by glass electrode potentiometric measurements. Measurements were made in absence and in the presence of either polyoxyethylene sorbitanmonolauerate (tween-20, 0.5%), polyethylene glycol tert—octylphenyl ether (triton-x 100, 0.5%), sodium n-dodecylsulphate (SDS, 10 mmol/L) or n-cetyl trimethylamonium bromide (CTAB, 1 mmol/L). The total concentrations of aluminium(III) ion used were 0.5, 1.0, 2.5 and 5.0 mmol/dm^3. Measurements were made in the pH interval between 2.5 and 4.8. The model comprising the species (1,-1), (3,-4) and (13,-32) constitutes the skeleton for all studied systems, in the pH interval 3.6 – 4.5. In addition to this model, to fit the data in 0.01 and 0.1 M LiCl medium it was necessary to include the soluble (1,-3) complex in a speciation scheme. This complex was also included in the presence of non-ionic surfactants. Re-dissolution of colloidal $Al(OH)_3$ is hindered in the presence of SDS and CTAB but in considerably lesser extent in the presence of tween and triton X-100. All surfactants used mainly exert influence on higher molecular weight hydrolytic species of aluminium. Non-ionic surfactants (tween-20 and triton-x 100) influence the hydrolysis only slightly in terms of the stability constants of the hydrolytic complexes. The ionic surfactants (SDS and CTAB) influence the hydrolysis considerably in terms of both, the speciation and the stability of the formed hydrolytic complexes. The speciation is significantly changed i.e. (1,-3) complex was not detected, while much higher values for the stability constants of (3,-4) and (13, -32) hydrolytic species were obtained, than in the pure ionic medium. These effects were explained by the hydrophobic/hydrophilic properties of the surfactants as well as their solubilizing power.

INTRODUCTION

Aluminium(III) ion in water solutions is very prone to hydrolysis [1]. The extent of hydrolysis, identity and stability of hydrolytic species formed in solution depend upon the nature and concentration of the supporting ionic medium, pH of the solution, the nature and concentration of the base used to force the hydrolysis, ageing time and the presence of other substances which may interact with aluminium(III) ion and/or water molecules. Therefore, a wide variety of experimental protocols and methods for the data treatment have been used in studying the aluminium hydrolysis [2]. As regards the potentiometric measurements of aluminium hydrolysis, two main approaches to the experimental protocol have been employed so far. First protocol is based on establishing of nearly true thermodynamic equilibrium in the solution while the other one is based on the measurements performed in metastable, steady state of the system. It is believed that thereby obtained speciation reflects one definite state of the system and that slow polymerization does not affect this state considerably. Titrations are performed either as continuous or batch. Taking into account slowness of the hydrolysis in the intermediate interval of pH (pH 4.0 – 4.5) batch titrations are advantageous, however, relatively small number of points and disturbance of standard electrode potential during the measurements limit the use of this method. Most frequently, continuous titrations were used. Their inherent drawbacks (diffusion, leak of reference electrode electrolyte, drift of potential) were mainly overcome by suitable experimental setup (use of Wilhelm's bridge, anti-diffusion tips, etc). Main difficulty in spite of everything, remains stability of electrode readings over a prolonged period of time needed for hydrolysis to go to completeness. Usually, potential of electrode is monitored every 1 – 2 min after addition of the titrant and it is somewhat arbitrarily decided that if the potential does not change more than 0.1 – 0.05 mV during 5 - 10 min, to proceed with titration. When permanent drift of potential is encountered or turbidity was observed either visually or by turbidimetry, the titration is stopped. For the purpose of data analysis only points obtained in true solution are selected.

There is no unique model for aluminium hydrolysis. The data accumulated so far indicate that at very low aluminium concentrations (micromolar) and in mildly acidic solutions (pH 3 – 5) mononuclear hydrolytic complexes, $Al(OH)^{2+}$ and $Al(OH)_2^+$ are formed, rapidly and reversibly, by splitting off the proton from the coordinated water molecules in aqua aluminium ion, $Al(OH_2)_6^{3+}$ [3]. Upon increasing the pH, further successive deprotonation leads to the formation of $Al(OH)_3$ and $Al(OH)_4^-$ [4]. When total aluminium concentration exceeds 1 μmol/L, amorphous $Al(OH)_3$ begins to precipitate. Minimum solubility of $Al(OH)_3$ is reached at about pH 6.2 – 7.4 (depending on the nature and concentration of the ionic medium) [5]. In the milimolar range of aluminium concentration, in the pH interval from 3 to 5, two basic hydrolytic models were derived: one put forward by Mesmer and Baes [6], which includes the complexes $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al_3(OH)_4^{5+}$, $Al_2(OH)_2^{4+}$ and $Al_{13}(OH)_{32}^{7+}$ and the other one, minimalistic, proposed by Ohman [7], which includes $Al(OH)^{2+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}(OH)_{32}^{7+}$ complexes. If hydrolysis of aluminium is carried out in higher concentration range of aluminium, (0.1 – 1 mol/L), without subsequent ageing, main hydrolytic products involve varying proportions of Al^{3+}, $Al_2(OH)_2^{4+}$ and $AlO_4Al_{12}(OH)_{24}^{7+}$ species [8]. Upon high dilution of these solutions dimmer is converted to the tridecamer [9]. At higher pH values, Al^{3+} solutions can be hydrolyzed extensively (up to hydrolysis ratio m = 2.5, where m is defined as the ratio: $[OH^-]$ added/total $[Al^{3+}]$) with the formation of polynuclear complexes of varying composition, depending on the way the hydrolysis is conducted. These solutions are supersaturated with respect to one or more solid hydrated oxides or amorphous hydroxide, $Al(OH)_3$. The rates of polymer formation are quite slow (minutes to months). These complexes may persist in solution for long periods of time as metastable species even if the actual pH of the solution corresponds to the conditions where they are no longer the most stable species. Total time of the reaction, hydrolysis agent, the temperature and nature of the supporting anion could modify not only relative concentrations of these species but also their composition. The model proposed by Brosset et al., [10] can accommodate a host of possible light polymeric species having a general formula $Al[Al_2(OH)_5]_n$, although some authors concluded that among all possible polymers only a few seemed to actually exist [11].

Solution behavior of higher hydrolytic polymers of aluminium as well as $Al(OH)_3$ (or hydrated aluminium oxide) can be modified not only by changing the temperature, ionic medium or ageing time but also, by the presence of surface active agents (SAA) or surfactants. These substances alter the properties of solution interfaces (solution-vapor, solution-solid, etc). Surfactant molecule is composed of hydrophilic group and hydrophobic moiety. The entire molecule is often referred to as amphiphilic because of its dual nature. They are generally classified as either anionic, cationic or nonionic according to the charge of their hydrophilic head group upon dissolution in water [12]. If sufficient surfactant is added to aqueous solution aggregation of its molecules occurs giving rise to the ordered structures called micelles. Micelles are often spherical in shape, but at larger concentration of SAA, they can take other, more distorted forms. The threshold concentration of SAA at which micelles begin to form is termed the critical micelle concentration (CMC) [13]. Other substances present in solution can partition into the interior of the micelle, thereby increasing the total aqueous solubility of the substance by a process referred to as micellar solubilization [14].

Hydrolytic polymers of aluminium and amorphous $Al(OH)_3$ show strong adsorption properties [15] so that in the presence of SAA they could become coated with molecules of SAA, intercalated into the interior of the micelles of SAA or involved in ion-dipole or ion-ion interactions with charged or polar part of SAA molecule. On the other hand, the molecules of SAA can interact with water thereby changing the availability of water molecules for hydrolysis. Thus, they could modify relative proportions and intrinsic nature of the various hydrolytic species present in solution. Their influence on aluminium(III) ion hydrolysis could conveniently be interpreted in terms of their solubilizing properties, protolytic tendencies of coordinated and bulk water molecules and electronic structure of aluminium(III) ion.

The effect of surface active substances on hydrolysis of aluminium(III) ion has been studied very little [16]. Quantitative results are not available in the literature. Therefore, in the present study we report on the hydrolytic properties of aluminium(III) ion in the presence of a number of surface active substances. For comparison purposes the hydrolytic measurements were also made in absence of SAA (surfactants). Bearing in mind that the CMC value of SAA depends on many factors such as, nature of SAA molecule, ionic medium, pH and the presence of other organic molecules in solution [17] investigation of the effect of SAA on hydrolysis of Al^{3+} ion was conducted under the same experimental conditions (i.e. pH interval, concentration range of aluminium, ionic medium, temperature and ageing time). Classical glass electrode potentiometric measurements were used as the most reliable for this kind of experiments.

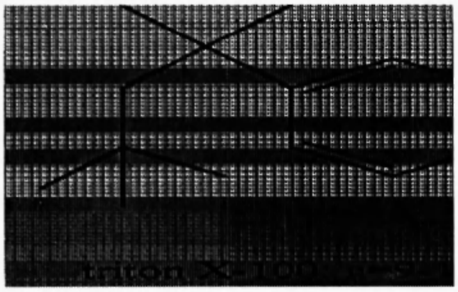
In this work we used anionic (SDS), cationic (CTAB) and nonionic (triton X-100 and tween-20) surfactants to investigate the hydrolytic behavior of aluminium ion in their presence. Surfactants used in the present study can mimic the action of natural phospholipids found in cellular membranes [18]. Since cellular uptake of aluminium(III) ion is dependent on hydrophilic/lipophilic properties of the cell membrane, here obtained results may be useful in understanding the metabolic transformations of aluminium in organism. Another important use of the results from this study is in the water purification technology. Aluminium salt (sulfate or chloride) is added to water in the process of purification and so produced aluminium hydroxide acts as a coagulant for various organic contaminants present in water [19]. Its coagulation properties can be significantly modified by the presence of either natural SAA (humic and fulvic acids) or others, subsequently added. Thus, the present study should address the problem of coagulation behavior of $Al(OH)_3$ in waters (i.e. highly diluted solutions).

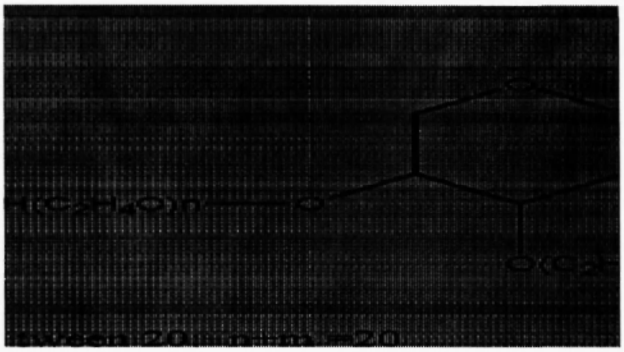
EXPERIMENTAL

Reagents and Analysis

The stock solution of aluminum(III) chloride was prepared by dissolving doubly recrystallized $AlCl3 . 6 H_2O$ p.a. (Merck) in twice distilled water. The appropriate amount of HCl was added to avoid initial hydrolysis of Al(III). The aluminum content was determined gravimetrically by the precipitation with 8-hydroxyquinoline or ammonia. Both methods gave the same results within 0.3%. The concentration of the free acid was determined potentiometrically using the Gran plot. The constancy of the total proton concentration with time was considered as a criterion for the absence of initial aluminum(III) hydrolysis and was periodically checked by titration against standard NaOH before each series of measurements.

The sodium hydroxide solution was prepared from a concentrated volumetric solution p.a. (Merck) by diluting with freshly boiled doubly distilled water, cooled under constant flow of purified nitrogen. The alkali concentration was checked by titration against potassium hydrogen phthalate. The hydrochloric acid solution was made from HCl "Suprapure" (Merck) and standardized against tris(hydroxymethyl) aminomethane. The solution of lithium chloride was prepared form LiCl, p.a (Merck) by dissolving the recrystallized salt in twice deionized water. The concentration was determined by evaporation of a known volume of solution to dryness at 573 K and weighing the residue.





Sodium n-dodecyl-sulfate (SDS), $CH_3(CH_2)_{11}OSO_3Na$, M_r = 288.4 and cetyltrimethylammonium bromide (CTAB), $[C_{16}H_{33}N^+(CH_3)_3]Br^-$, M_r = 364.5, were products of Sigma (USA) while polyoxyethylene sorbitanmonolaureate (tween 20), M_r = 1322.5, and polyethylene glycol tert-octylphenyl ether (triton X-100), M_r = 647, were products of Fluka (Austria). Their general formulae are:

Before use SDS was purified by washing with ether and 95% ethanol and subsequently dried in a desiccator containing P_2O_5.CTAB was washed with ethanol and recrystallized from water. Traces of polyethylene - glycols in tween and triton were removed by extraction with n-buthanole. Purity of surfactants was checked with TLC and spectrophotometry, according to recommended procedure [16,20] and by measurement of pH of their water solution. No basic impurities were detected.

Equipment

Potentiometric measurements were carried out using a Tacussel Isis 20000 digital pH-meter with a precision ± 0.1 mV (in some measurements an extended scale was used with a precision ± 0.01 mV). The pH meter was equipped with a Tacussel TC-100 combined electrode. Titrant was delivered from a Metrohm Dosimat model 665. A constant temperature was maintained with a VEB Prufgerate model E3E circulating ultrathermostat.

Procedure

All titrations were performed in a double mantled, thermostated glass vessel closed with a Teflon cork. The constant temperature (298.0 + 0.1 K) was maintained by circulating the thermostated water through the jacket. Purified and oxygen free nitrogen gas was bubbled through the solution for providing an inert atmosphere and stirring. Additional stirring of the solution was achieved with a magnetic stirrer.

The electrochemical cell used for the potentiometric measurements may be represented as: RE/test solution (TS)/GE where RE and GE denote reference and glass electrode respectively. The general composition of the test solution was: $TS = M$ Al(III), H H^+, X Cl^- , C (surfactant), where M, H, X and C denote total molar concentrations of corresponding species. X was 0.01, 0.1 and 1.0 mol/dm^{-3}, while C was chosen in such way to be slightly higher than the critical micellar concentration.

The potential of the glass electrode is given by the expression:

$E = E_0 + Q \log h + E_j$

where h is the concentration of free protons, E_0 is a constant which includes the standard potential of the glass electrode, Q is the slope of the glass electrode response and E_j is a liquid junction potential whose contribution to E was found to be negligible. The E_0 was determined both before and during each titration of the test solution. First, E_0 was determined by means of a separate titration of HCl with sodium hydroxide, both of known concentrations, under the same medium and temperature conditions as the test solution titrations (1.0, 2.5 and 5.0 mmol/dm^3 HCl was titrated with 0.100 mol/dm^3 NaOH). The data so obtained were analyzed with the aid of the Magec [21] program. The calculated values of Q and the auto-protolysis constant of water, pK_W were in agreement with literature data [22] thus confirming reliability of the experimental setup. During the titrations of the test solutions, the E_0 was determined using the data in acidic medium, where no hydrolysis takes place ($h = H$), by plotting the value $E - Q \log h$ against h and extrapolating the straight line so obtained to $h = 0$. When the difference between two E_0 values was higher than 2.0 mV, the titration was rejected. Thus, the obtained value of E_0 was used for the calculation of $-\log h$ for the whole titration curve.

To reduce the concentration of the hydrogen ion, the titrant was added stepwise from an auto-burette in small aliquots (0.005 - 0.01 mL). A standard NaOH solution prepared in a corresponding ionic medium was used as titrant. During the titration the potential was monitored after each addition of a titrant. The readings were taken every 2 min until steady values to ± 0.1 mV/min were obtained. Hence, the average equilibration time (when hydrolysis occurred) for each point in hydrolysis measurements was 15 - 20 min, so that most titrations lasted 12 – 16 hr. However, in 0.01 mol/L LiCl medium it was necessary to wait considerably longer for steady values of potential readings to be attained so that these titrations lasted approximately two days. The titrations were terminated when drifted potential readings were obtained and turbidity of solutions observed. Some titrations were carried in duplicate and some in triplicate. Only the titrations that showed agreement between duplicate measurements better than 5%, constancy of the measured potential to ± 0.1 mV (or ± 0.002 pH units) over prolonged period of time as well as constancy of E_0, were used in calculations.

RESULTS AND DISCUSSION

The experimental data obtained in the 0.01, 0.1 and 1.0 mol/dm^3 LiCl medium, at 298 K are summarized in Table 1.

The maximum value of average hydroxide number, Z, defined as $Z = (h - H)/M$, was between 0.40 – 0.55, depended on the kind of surfactants present. The data shows that for each concentration of the aluminum studied, a separate titration curve, $Z = Z(-\log h)$ was obtained. This indicates the formation of polynuclear hydrolytic complexes. The pH region in which hydrolysis occurs depends upon the total concentration of aluminum, concentration of ionic medium and the nature of the surfactant (Fig. 1). As the concentration of the aluminium(III) ion increases, the beginning of hydrolysis shifts towards lower pH values, while at the same time the degree of hydrolysis decreases.

Possible complexation of aluminum(III) ion with chloride from the ionic medium, should appear as a constant effect because of relatively high concentration of the medium; therefore, it should not affect the number of hydroxide ions bound to aluminum. Though the titrations were performed in a wide pH range, for the purpose of calculations some reduction of the number of titration points was necessary. Points at low pH values, where hydrolysis is negligible and at pH's higher than 4.5, where solutions became turbid and colloid formation may take place, were excluded from calculations. Thus, only points obtained in clear solutions were taken into calculations.

Table 1. Summary of potentiometric data on aluminum(III) hydrolysis in 0.01, 0.1 and 1.0 mol/dm^3 LiCl ionic medium, at 298 K. Concentrations C_x, of the corresponding species are given in mmol/dm^3. Z_{max} is the maximum value of the average hydrolytic number attained.

Entry	C_{Al}	C_{HCl}	C_{SDS}	C_{CTAB}	C_{tween}	C_{triton}	pH range	Z_{max}
				0.01 mol/dm^3 LiCl				
1	0.5	2.92	-	-	-	-	2.644-4.667	0.464
2	1.0	3.03	-	-	-	-	2.645-4.592	0.420
3	0.5	3.31	10.0	-	-	-	2.433-4.223	0.500
4	1.0	2.94	10.0	-	-	-	2.410-4.258	0.301
5	0.5	2.99	-	1.0	-	-	2.689-4.749	0.456
6	1.0	3.14	-	1.0	-	-	2.678-4.548	0.310
7	0.5	2.92	-	-	0.5	-	2.611-4.612	0.537
8	0.5	2.93	-	-	-	0.5	2.610-4.640	0.572
9	1.0	3.02	-	-	-	0.5	2.629-4.544	0.487
				0.1 mol/dm^3 LiCl				
10	1.0	3.03	-				2.566-4.555	0.489
11	2.5	3.04	-				2.582-4.382	0.248
12	5.0	3.05	-				2.557-4.312	0.398
13	10.0	2.86	-				2.575-4.170	0.200
14	1.0	2.96	10.0				2.445-4.258	0.290
15	2.5	3.25	10.0				2.561-3.898	0.159
16	1.0	3.07		1.0			2.528-4.453	0.211
17	2.5	3.07		1.0			2.522-4.236	0.101
18	5.0	3.05		1.0			2.615-4.204	0.135
19	1.0	2.96			0.5		2.622-4.590	0.537
20	5.0	2.96			0.5		2.655-4.370	0.376
21	10.0	2.80			0.5		2.574-4.190	0.224
22	1.0	3.01				0.5	2.644-4.590	0.493
23	5.0	2.92				0.5	2.676-4.258	0.328
24	10.0	3.05				0.5	2.662-4.206	0.202
				1.0 mol/dm^3 LiCl				
25	1.0	2.56					2.316-4.359	0.434
26	2.5	2.55					2.359-4.168	0.394
27	5.0	2.49					2.286-3.977	0.322
28	1.0	2.56	10.0				2.641-4.243	0.231
29	2.5	2.55	10.0				2.268-3.688	0.147
30	1.0	2.56		1.0			2.435-4.425	0.231
31	2.5	2.55		1.0			2.430-4.243	0.295
32	5.0	2.49		1.0			2.565-4.174	0.155
33	1.0	2.86				0.5	2.426-4.397	0.549
34	5.0	3.02				0.5	2.458-4.192	0.364
35	10.0	2.91				0.5	2.472-4.015	0.215

Reacting with water molecules, the aluminum(III) ion forms one or more hydrolytic complexes of the general composition $Al_p(OH)_q^{(3p - q)+}$ (further abbreviated as (p,q)) whose overall formation constants, $\beta_{p,q}$ can be defined as:

$$\beta = C_{p,q} m^{p} h^{q}$$

where $C_{p,q}$ denotes the equilibrium concentration of the (*p,q*) complex and *m* is the free concentration of Al^{III} ion. In the above reaction, the chloride ions and water molecules are omitted from the coordination sphere.

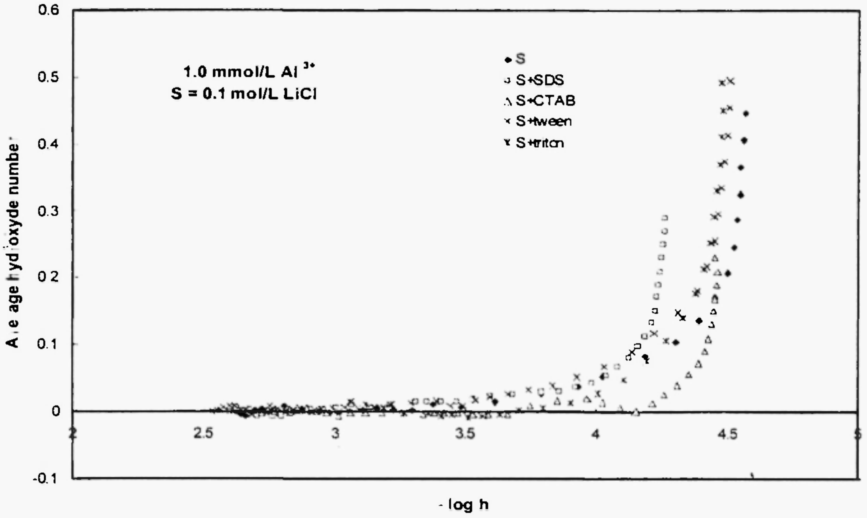


Figure 1. Hydrolysis of aluminium(III) ion in absence and in the presence of surface active substances. The concentrations of surfactants were: SDS = 8 mmol/L, CTAB = 1mmol/L, tween20 = 0.6 mmol/L, triton100= 0.4 mmol/L

First, each titration curve was processed separately using the program Best [23]. On the basis of hydrolytic curves *Z = Z(- log h)*, the *p*H interval chosen was 3.5 – 4.4 - 4.5 (depending on ionic medium) . Complexes from the initial set comprising (1,-1), (1,-2), (1,-3), (1,-4), (2,-1), (2,-2), (2,-3), (2,-4), (2,-6), (3,-3,), (3,-4), (3,-6), (6,-12), (6,-15), (6,-18), (8,-12) and (13, -32) were introduced one at a time until the minimum value of σ_{fit} [6] was obtained. During the calculations all the titration parameters (M_0, H_0) were kept constant while *p*H values in repeated cycles of calculations were adjusted until the best possible value of σ_{fit} was obtained. Then all titration curves relating to definite medium concentration and the surfactant were processed together, this time using the program Superquad [24].

In Superquad calculations the identity and stability of complexes which give the best fit to the experimental data, were determined by minimizing the error-squares sum of the potentials, *U*:

$$U = \quad w_i(E_{obs} - E_{calc})^2$$

where w_i represents a statistical weight assigned to each point of titration curve, E_{obs} and E_{calc} refer to the measured potential of the cell and the calculated one assuming the specific model and trial constants, respectively. The best model was chosen using these criteria: (a) the lowest value of *U*, (b) standard deviation in calculated stability constants less than 0.15 log units, (c) standard deviations in potential residuals, defined as:

$$s = \{ewe' \,/\, (N-k)\}^{1/2}$$

where e is a vector in potential residuals (E_{obs} - E_{calc}), *w* is a weighting matrix, *N* is the number of observations and *k* is the number of refinable parameters, with standard deviation in volume readings 0.0005 cm^3 and standard deviation in potential readings 0.1 mV, should be less than 3.0. (d) goodness-of-fit statistics, χ^2 (Pearson's test) at 95% confidence level, with 6 degrees of freedom, less than 12.6 and (e) reasonably random scatter of potential residuals without any significant systematic trend.

During the Superquad calculations the E_0 values were allowed to float while all analytical parameters were held constant. The final results of calculations are given in Table 2 together with the calculated statistical parameters, χ^2 and s.

Table 2. Stability constants of hydrolytic complexes formed in 0.01 mol/dm^3, 0,1 mol/dm^3 and 1 mol/dm^3 LiCl ionic medium, at 298 K in absence and in the presence of surface active substances.

Species	$-\log \beta_{p,q}$				
	S = 0.01 mol/dm^3 LiCl				
	S	S + tween	S + triton	S + SDS	S + CTAB
(1,-1)	5.12 ± 0.02	5.18 ± 0.05	5.31 ± 0.02	4.75 ± 0.03	5.09 ± 0.03
(1,-3)	14.54 ± 0.03	14.56 ± 0.02	14.54 ± 0.06	-	-
(3,-4)	13.31 ± 0.12	13.26 ± 0.05	13.50 ± 0.02	12.18 ± 0.02	13.25 ± 0.09
(13,-32)	108.28 ± 0.1	108.00 ± 0.09	108.58 ± 0.06	102.0 ± 0.05	106.06 ± 0.06
χ^2	11.0	8.0	11.0	12.29	8.0
S	1.09	1.2	1.1	1.5	1.2
S = 0.1 mol/dm^3 LiCl					
(1,-1)	5.27 ± 0.01	5.21 ± 0.02	5.43 ± 0.04	4.88 ± 0.04	5.25 ± 0.01
(1,-3)	14.68 ± 0.03	14.66 ± 0.02	14.63 ± 0.06	-	
(3,-4)	13.81 ± 0.02	13.43 ± 0.14	13.58 ± 0.07	12.34 ± 0.02	13.48 ± 0.01
(13,-32)	109.23 ± 0.06	108.5 ± 0.1	108.72 ± 0.07	103.93 ± 0.03	107.34 ± 0.08
χ^2	11.1	12.4	12.2	12.35	12.6
S	1.2	1.1	3.6	2.0	1.1
S = 1 mol/dm^3 LiCl					
(1,-1)	5.36 ± 0.03	-	5.52 ± 0.05	5.05 ± 0.04	5.33 ± 0.01
(3,-4)	13.99 ± 0.05	-	13.74 ± 0.02	12.44 ± 0.04	13.58 ± 0.02
(13,-32)	111.6 ± 0.07	-	109.14 ± 0.1	107.23 ± 0.09	111.42 ± 0.07
χ^2	11.88	-	11.9	10.2	12.66
S	1.0		1.6	2.9	1.0

Our model for aliminium(III) ion hydrolysis in 1 mol/dm^3 LiCl medium, is in agreement with that found by Ohman et al. [25,26]. Values of the corresponding stability constants are compared in Table 3.

Table 3. Stability constants of aluminium(III) ion hydrolytic complexes ($-\log \beta_{p,q}$)

Species	This work^a	Ref 25^b	Ref. 26^c
$Al(OH)^{2+}$	5.36 ± 0.03	5.52 ± 0.04	5.52 ± 0.5
$Al_3(OH)_4^{5+}$	13.99 ± 0.05	13.57 ± 0.02	13.96 ± 0.01
$Al_{13}(OH)_{32}^{7+}$	111.6 ± 0.07	109.2 ± 0.2	113.35 ± 0.13

^{a} 1 M LiCl medium, 25^{0}C, ^{b} 0.6 M NaCl, 25^{0}C, ^{c} 3 M NaCl medium, 25^{0}C

In 0.1 M and 0.01 M LiCl medium in addition to the complexes found in 1 M LiCl medium the "soluble" hydrolytic complex $Al(OH)_3$ appears in a speciation scheme. The calculated stability constants are in fair agreement with that found by Nazarenko and Nevskaya [27] ($-\log \beta_{1,-3}$ = 15.6, 0.1 M $NaClO_4$, 25^{0}C). Appearance of the "soluble" $Al(OH)_3$ in hydrolytic schemes at lower ionic strengths may be a consequence of the higher concentration of water available for hydrolysis and possibly, colloidal peptization of amorphous, finely dispersed, aluminium hydroxide. The calculation showed that along with $Al(OH)_3$ complex in 0.01 and 0.1 mol/dm^3 LiCl medium, in the presence of non-ionic surfactants, the complex $Al(OH)_2^+$ can be included in speciation scheme. Inclusion of the diol led to the rejection of $Al(OH)_3$ with worse set of statistical parameters. Improvement of statistics could have been achieved with the inclusion of the dimmer $Al_2(OH)_2^{4+}$. Inclusion of other hydrolytic polymers led to either their rejection or very bad set of statistics. Since however, Pearson's test was much closer to the expected (theoretical) value with the models which do not include the $Al(OH)_2^+$ complex, it was excluded from the final speciation schem

The influence of the surfactants on the stability on the hydrolytic complexes formed in solution can be conveniently expressed in terms of the difference between stability constant in pure ionic medium and in the medium containing the surfactant i.e., higher $\Delta\log\beta$ (= $\log\beta_{(S)} - \log\beta_{(S+D)}$ values, where D stands for detergent). The data are given in Table 4.

Table 4. Differences in stability constants of (p,q) hydrolytic complexes: $\Delta\log\beta_{p\,q} = \log\beta_{(S)} - \log\beta_{(S+D)}$, where S stands for pure ionic medium and D denotes detergent (surfactant).

Surfactant	$\Delta\log\beta_{p,q}$		
	S = 0.01 M LiCl	S = 0.1 M LiCl	S = 1.0 M LiCl
(1,-1)			
SDS	-0.37	-0.39	-0.31
CTAB	-0.03	-0.02	-0.03
Tween	0.06	-0.06	-
Triton	0.19	0.16	0.16
(3,-4)			
SDS	-1.13	-1.47	-1.55
CTAB	-0.06	-0.33	-0.41
Tween	-0.05	-0.38	-
Triton	0.19	-0.23	-0.25
(13,-32)			
SDS	-6.28	-5.30	-4.36
CTAB	-2.22	-2.11	-0.18
Tween	- 0.28	- 0.73	-
Triton	0.30	-0.51	-2.46

As seen from the table 4 in all concentrations of the supporting ionic medium, the influence of ionic surfactants (SDS and CTAB) on the stability constants is higher than the neutral ones. The effect of surfactants is considerably higher on hydrolytic oligomer (3,-4) and the polymer (13,-32) than on the mononuclear hydroxo complex (1,-1). The SDS exerts the highest influence on the stability of hydrolytic complexes, and this influence rises as the concentration of the ionic medium increases. In Fig. 2 the distribution of the hydrolytic species in 0.1 mol/dm^3 LiCl medium in the absence and in the presence of SDS is shown.

It is obvious from Fig. 2. that in the presence of SDS the concentration of (1,-1) and (13,-32) complexes increase with the shift of maximum concentration toward lower pH values. Also, in the presence of SDS, the formation of $Al(OH)_3$ in "soluble" form, at pH values between 4.0 and 4.5 was not detected probably because of fast conversion of low molecular weight species to the tridecamer.

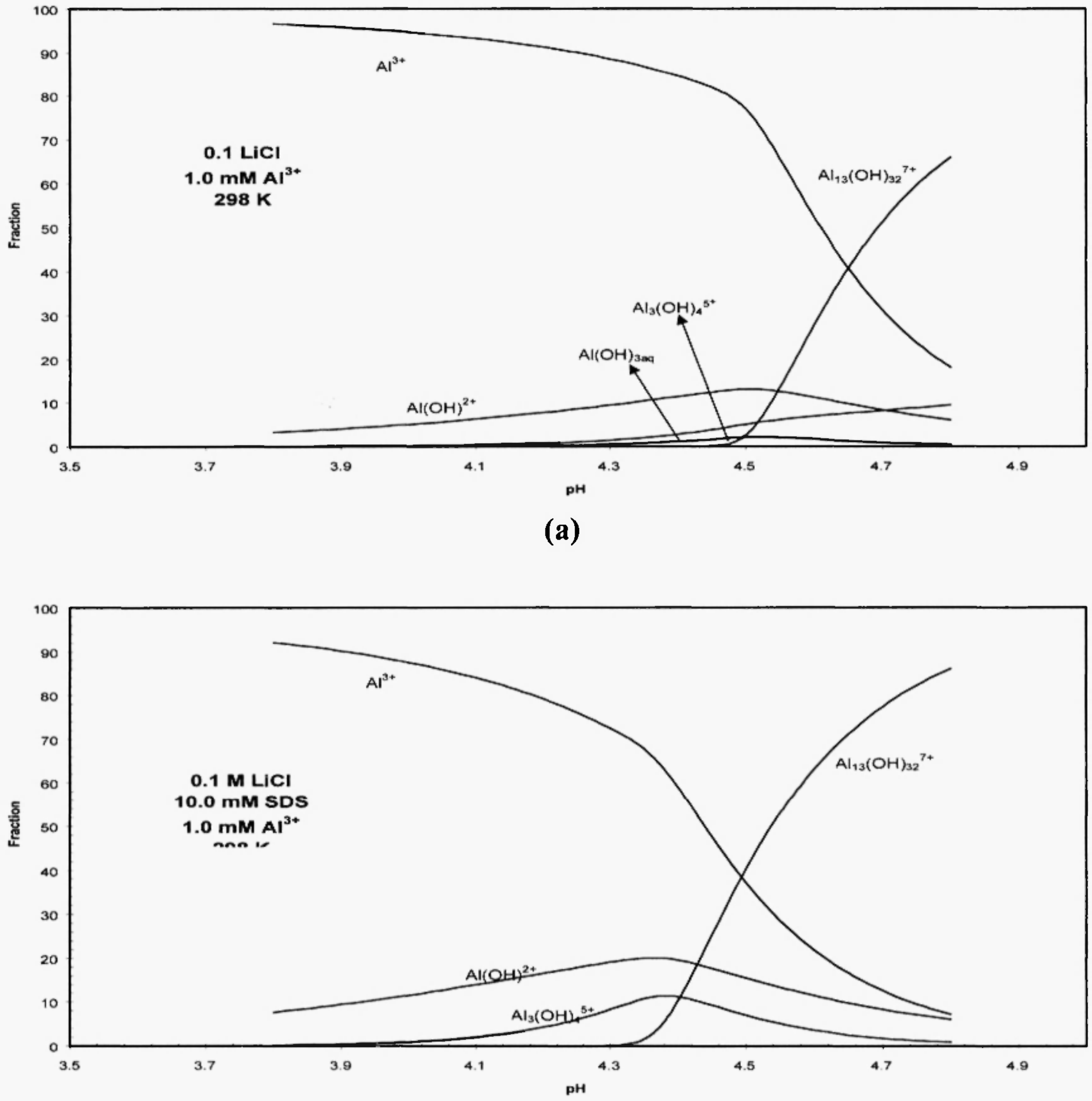
To explain the observed phenomena in Table 5 are shown some characteristics of the surfactants together with the stability constants of (3,-4) and (13,-32) species, in 0.1 mol/dm^3 LiCl ionic medium.

As seen from table 3 the CMC and aggregation number of the surfactants do not correlate with the stability constants of the hydrolytic species. However, the HLB number shows good correlation with the stability constant of the tridecamer, (13, -32) and (3,-4) species (Fig. 3).

The correlation is linear:

$$p\beta_{p,q} = A - B \times \text{HLB}$$

with A = 111.3 ± 0.3, B = 0.18 ± 0.01, and correlation coefficient r = 0.997 for (13,-32) complex and A = 14.3 ± 0.1, B = 0.05 ± 0.01 and r = 0.985 for (3,-4) complex. Similar correlation can be found for both, (3,-4) and (13,-32) species in 0.01 M LiCl medium, but with rather scattered points and r being less than 0.8. Since HLB value reflects solubilizing property of the surface active substance it follows that the effect of SDS, CTAB, tween and triton on hydrolysis of aluminium(III) ion could be interpreted in terms of their solubilizing power.



(a)

(b)

Fig. 2. The distribution of aluminium(III) hydrolytic species in the absence (a) and in the presence (b) of sodium dodecylsulfate (SDS).

Table 5. Characteristics of the surface active substances [28]. The CMC denotes critical micellar concentration (mmol/dm^3), HLB stands for hydrophilic-lipophilic balance value, while AGG denotes aggregation number of micelles.

Surfactant	CMC	AGG	HLB	- log $\beta_{p,q}$	
				(3,-4)	(13,-32)
Tween 20	0.05	-	16.7	13.43	108.5
Triton X100	0.24	140	13.58	13.58	108.72
SDS	8.2	62	40	12.34	103.93
CTAB	1.0	169	20	13.48	107.34
0.1 M LiCl	-	-	-	13.81	109.23

Aggregation number represents average number of individual surfactant molecules in the micelle. The hydrophile-lipophile balance number (HLB) is a measure of the relative strength of hydrophilic and hydrophobic parts of the surfactant molecule [28]. HLB numbers characterize the relative affinity of SAA for aqueous and non-polar phases. The SAA which have higher HLB numbers will show good solubilizing power for less hydrophobic substances dispersed in water [28].

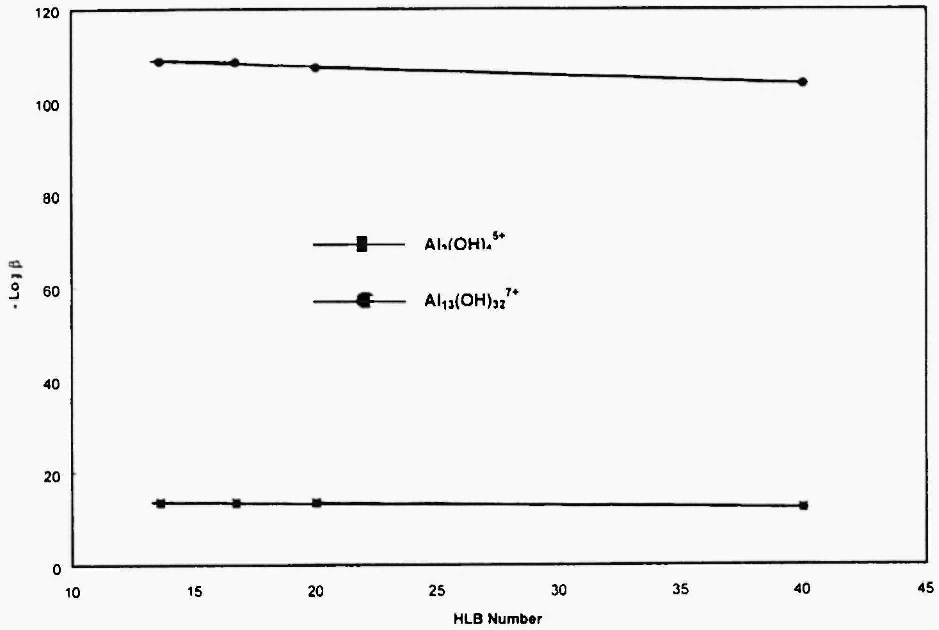


Fig. 3. Correlation between the stability constant of (13,-32) and (3,-4) hydrolytic species and HLB number of surfactants.

This is the most pronounced for SDS and consequently, it possesses the strongest effect on hydrolysis. Its negatively charged polar heads surround the hydrolytic species in a spherical micelle and thus shift the hydrolytic equilibrium to the right. The partition of the species inside the micelle increases with the charge of the species and its diameter i.e. its area to volume ratio. The other surfactants behave similarly, but because of their lower HLB value the effect is also lower. The mechanism described may be partly responsible for transportation of aluminium (not bound to transferrin) into the cell [29]. Hydrolytic species of aluminium at physiological pH should be mainly, tridecamer and $Al(OH)_4^-$ which may partition into the cell membrane phospholipid micelles and thus transported into the cell.

Hydrolyzed Al^{3+} solutions can be appreciably supersaturated with respect to $Al(OH)_3(aq)$ as seen from Table 2. Hydrated $Al(OH)_3$ eventually begins to precipitate in the form of amorphous $Al(OH)_{3(s)}$ at pH values higher than 4.0. Exact composition of the precipitate may vary in dependence on supporting ionic medium, ageing time, the presence of foreign substances, etc. In chloride ionic medium it may be supposed that the formation of the precipitate [30] proceeds according to equilibrium:

$$AlCl_n + m\ H_2O \rightleftarrows Al(OH)_mCl_{n(s)} + (3\text{-}n)\ Cl^- + m\ H^+$$

with the equilibrium constant K_e and $m + n = 3$. Stepwise formation of chloro-complexes of aluminium takes place according to reaction:

$$Al^{3+} + n\ Cl^- \leftrightarrows AlCl_n^{3-n}$$

with the equilibrium constant, K_n.

From these two equilibria the constant K_e may be expressed as:

Equation 1:

$$K_e = \frac{h^m[Cl^-]^3}{K_n[Al^{3+}][H_2O]^m}$$

Assuming that the concentration of chloride is constant in 1 mol/dm^3 LiCl, as well as that of water, one obtains form eq. 1:

Equation 2:

$$K_{eq} = K_n K_e [H_2O]^m [Cl^-]^{-3} = \frac{h^m}{[Al^{3+}]}$$

where h denotes free concentration of the hydrogen ion. Taking logarithms of both sides of eq. 2 one obtains:

Equation 3:

$$\log K_{eq} = m \log h - \log[Al^{3+}]$$

Differentiation of both sides of eq 3 yields:

Equation 4:

$$\frac{f \log[Al^{3+}]}{f \log h} = m$$

In order to determine *m* one must know the pH value at which the precipitation begins. It may be obtained [31] by back extrapolation of nearly vertical part of hydrolytic curve $Z = Z(-\log h)$ until intercept with $-\log h$ axis (Fig. 4) .

Inserting so obtained value of $\log h_p$ into eq 4 and plotting $\log [Al^{3+}]$ against $\log h_p$ a straight line is obtained with the slope equal *m*. Free concentration of aluminium, $[Al^{3+}]$ at h_p was obtained from the equation 5:

Equation 5:

$$C_{Al} = [Al^{3+}] + \quad p[Al_p(OH)_q]$$

which was solved for $[Al^{3+}]$ with the aid of the program Species [32]. Results of calculations are given in table 6.

The composition of the precipitate varies from $Al(OH)_{2.2}Cl_{0.8}$ in 1 mol/dm^3 LiCl to $Al(OH)_{1.2}Cl_{1.8}$ in the presence of SDS. It is seen from table 6 that SDS possesses the strongest influence on composition of the precipitate. This influence weakens in going to CTAB and Triton (in this order).

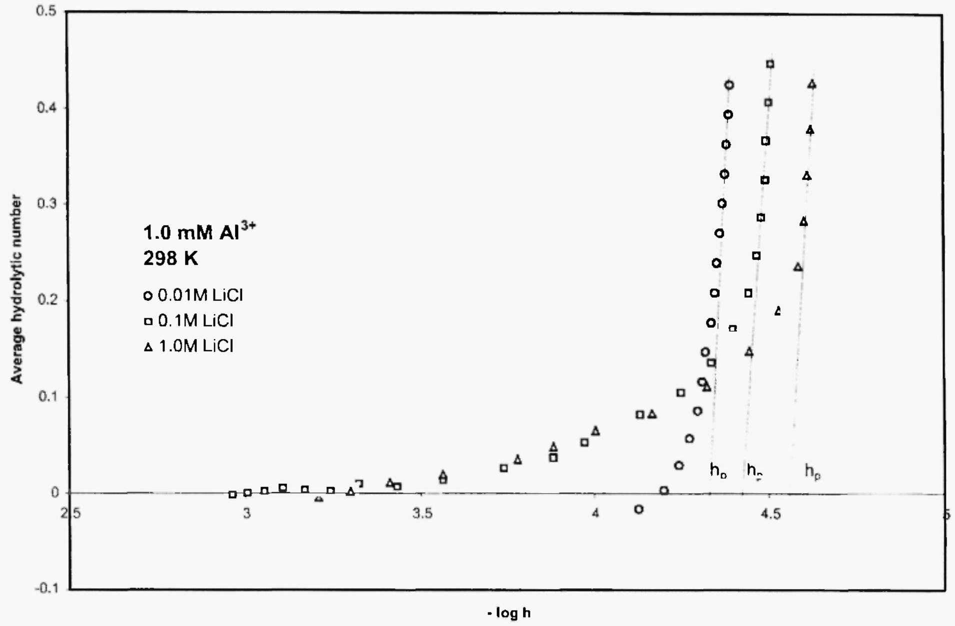


Fig. 4. Determination of beginning of hydrolytic precipitation in hydrolyzed Al^{3+} solutions

Table 6. Values of the coefficients *m* and *n* in $Al(OH)_mCl_n$, in different media

Medium	*m*	*n*
1 mol/dm^3 LiCl (S)	2.2	0.8
S + SDS	1.2	1.8
S + CTAB	1.8	1.2
S + Triton X-100	2.6	0.4

Instead of precipitation it is customary to consider re-dissolution of $Al(OH)_{3(s)}$, according to equilibrium:

$$Al(OH)_{3(s)} + 3\,H^+ \rightleftarrows Al^{3+} + 3\,H_2O$$

with the equilibrium constant, K_R. This constant can be calculated by the procedure described above. The results are given in table 7.

Table 7. Values of equilibrium constant, K_R, for dissolution of $Al(OH)_{3(s)}$ in various media at 25^{0}C. Total aluminium concentration in solution is 1 mmol/dm^3. M = mol/dm^3.

Medium	- log h_p	[Al^{3+}] (mmol/dm^3)	K_R
0.01 M LiCl	4.362	0.810	0.99×10^{10}
0.1 M LiCl (S)	4.476	0.796	2.13×10^{10}
1.0 M LiCl	4.642	0.627	5.28×10^{10}
S + SDS	4.210	0.785	0.33×10^{10}
S + CTAB	4.440	0.804	1.68×10^{10}
S + Triton X-100	4.439	0.842	1.75×10^{10}
S + Tween	4.472	0.765	2.00×10^{10}

As seen from table 7 the SAA shift the re-dissolution equilibrium to the left; the SDS exhibits the most pronounced effect. The K_R is almost 7 times lower in the presence of SDS than in the pure ionic medium.

The colloidal micelle of $Al(OH)_3$ in solution may be schematically represented as:

$$\{p[Al(OH)_3] \bullet q\, Al^{3+} \bullet 3\,(q - x)\, Cl^-\} \bullet 3x\, Cl^-$$

The ζ-potential determining ions are Al^{3+}[19] Chloride acts as counterion, but as a whole the micelle is charged positively. Anionic SAA, SDS destabilizes such structure of the micelles favoring their fusion and flocculation. Attack of H^+ is hindered resulting in shift of dissolution equilibrium of $Al(OH)_3$ to the left. Non-ionic SAA show protective effect on colloidal $Al(OH)_3$ probably by adsorption on the surface of the nucleus of $Al(OH)_3$ micelle. Generally, the SDS facilitates the deprotonation of water molecules form aqua Al^{3+} ion in true solution, but once soluble or colloidal $Al(OH)_3$ is formed, it decreases its ζ-potential and alleviates its growth and flocculation.

REFERENCES

1. C. F. Baes, Jr., R. E. Mesmer, *The Hydrolysis of Cations,* John Wiley, N. Y.. 1976., pp.112-123; C. Orvig, *The Aqueous Coordination Chemistry of Aluminum* in G. H. Robinson (ed.), *Coordination Chemistry of Aluminum,* VCH, Weinheim, 1993; J. W. Akitt, *Prog. Nucl. Magn. Res. Spectr.* **2 1** (1989)1-149; *Polyhedron. Symposium-in-Print no.10.* **9** (1990); P. M. Bertsch in G. Sposito (Ed.), *Environmental Chemistry of Aluminum*, CRC, Boca Raton. 1989, pp. 87-115
2. L.-O. Öhman, S. Sjöberg, *Coord. Chem. Rev.,* **149** (1995) 33-57; J. Havel, J. Meloun, *Computation of Solution Equilibria II. Potentiometry. Folia Fac. Sci. Natur. Univ. Purkynianae Brunensis* **26** (1985) 7-145; H. Rossotti, *The Study of Ionic Equilibria,* Longman, London, 1978, M. Beck, I. Nagypal, *Chemistry of Comples Equilibra,* Akademiai Kiado, Budapest, 1989. Chapter 4.
3. R. Bruce Martin, *Bioinorganic chemistry of aluminum,* in H. Sigel (ed.), *Metal Ions in Biological Systems. Vol. 24. Aluminum and its Role in Biology.* Marcel Dekker, New York and Basel, 1-57, 1988; W. R. Harris, G. Berthon, J. Philip Day, Ch. Exley, T. Flatten, W. F. Forbes, T. Kiss, C. Orvig, P. F. Zatta, *J. Toxicol. Environ. Health,* **48** (1996) 543-568; R. Bruce Martin, *J. Inorg. Biochem.,* **44** (1991) 141-147; E. Grunwald, Dodd-Wing, *J. Phys. Chem.,* **73** (1969) 650.
4. L.-O. Öhman, *Inorg. Chem.,* **27** (1988) 2565-2570; L.-O. Öhman, S. Sjöberg, N. Ingri, *Acta Chem. Scand.,* **A37** (1983) 561-568; M. Venturini, G. Berthon, *J. Chem. Soc. Dalton Trans.,* (1987) 1145-1148; S. Dayde, *Etude des equilibres de complexation et speciation simulee de la fraction ultrafiltrable de l'aluminium dans le plasma sanguine et la fluide gastro-intestinal. Implications pour la toxicite de l'aluminium.* These de Doctorat de l'Universite Paul Sabatier. Toulouse, 1990; Q. Chen, Y. Xu, L. G. Hepler, *Can. J. Chem.,* **69** (1991) 1685-1690.
5. H. Kubota, *Diss. Abstr.,* **16** (1956) 864
6. R. E. Mesmer, C. F. Baes, Jr., *Inorg. Chem.,* **10** (1971) 2290-2296
7. L.-O.Öhman, *Equilibrium Studies of Ternary Aluminium(III) Hydroxo Complexes with Ligands Related to Conditions in Natural Waters,* Ph. D. Thesis, University of Umeå, Umeå, 1983.
8. J. M. Elders, *NMR Studies of the Polymeric Cations Produced by the Hydrolysis of Aqueous Aluminium(III) Salt Solutions,* Ph. D. Thesis, University of Leeds, Leeds, 1986; J. W. Akitt, J. M. Elders, *J. Chem. Soc. Dalton Trans.,* (1988) 1347-1355; J. W. Akitt, A. Farthing, *J. Chem. Soc. Dalton Trans.,* 1617-1623 (1981); J. W. Akitt, A. Farthing, *J. Chem. Soc. Dalton Trans.,*1624-1628 (1981); J. W. Akitt, J. M. Elders, *J. Chem. Soc. Faraday Trans.,* **81** (1985) 1923-1930.
9. J. W. Akitt, J. M. Elders, *Bull. Soc. Chim. Fr.,* (1985) 10
10. C. Brosset, G. Biedermann, L. G. Sillen, *Acta Chem. Scand.,* **8A** (1954) 1917
11. C. Changui, W.E.E. Stone, L. Vielvoye, J. M. Dereppe, *J. Chem. Soc. Dalton Trans.,* (1990) 1723-1726; P. L. Brown, R. N. Sylva, G. E. Batley, J. Ellis, *J. Chem. Soc. Dalton Trans.,* (1985) 1967-1970; Ph. Charlet, J. P. Deloume, G. Duc, G. Thomas David, *Bull. Soc. Chim. Fr.,* (1984) 222-226.
12. B. Kueper, M. Pitts, T. Simpkin, T. Sale, *Technology Practices Manual for Surfactants and Cosolvents,* Rice Univ., Houston, 1997, Chapter 4; A. Abramzon, *Poverhnostno-aktivnye veschestva (Surface Active Substances),* Khimiya, Leningrad, 1981.
13. D. A. Sabatini, R. C. Knox, J. H. Harwell (Eds.), *Surfactant-Enhanced Subsurface Remediation,* ACS Symposium Series 594, American Chemical Society, Washington, 1995.

14. P.H. Elworthy, A. T. Florence, C. B. MacFarlane, *Solubilization by Surface Active Agents,* Chapman and Hall, London, 1968;
15. W. Stumm, J. J. Morgan, *Aquatic Chemistry,* Wiley Intersci., N.Y., 1970, pp. 445-512.
16. S.B. Savvin, R. K. Tshernova, S. N. Shtykov, *Analiticheskie Reagenty. Poverhnostno-aktivnye veschestva (Analytical Reagents. Surface Active Substances)*, Nauka, Moskva, 1991.
17. M. J. Rosen, *Surfactants and Interfacial Phenomena,* 2nd Edition, J. Wiley and Sons, New York, 1989.
18. A. A. Boldyrev, *Biologicheskie Membrany and Transport Ionov (Biological Membranes and Ion Transportation)*, Izd. Moskovsogo Univ., 1985.
19. J. Y. Bottero, J. L. Berisllon, *Aluminium and Iron(III) Chemistry: Some implications for organic substances removal* in I. H. Suffet, P. MacCarthy (Eds.), *Aquatic Humic Substances - Influence on Fate and Treatment of Pollutants,* Advances in Chemistry Series 219, American Chemical Society, Washington, 1989, pp. 425-442.
20. K. Toel, S. Motomizu, T. Umano, *Talanta* **29** (1982) 103-106; W. Selig, Z. Fresenius, *Anal. Chem.*, **300** (1980) 183-188.
21. P. W. Linder, R. G. Torington, D. R. Williams, *Analysis Using Glass Electrode,* Open University Press, Milton Keynes, 1984.
22. L. G. Sillen, A. E. Martell, *Stability Constants of Metal Ion Complexes,* Spec. Publ. XVII (1964) and XXV (1971). The Chemical Society, London.
23. A. E. Martell, R. J. Motekaitis, *Determination and Use of Stability Constants,* VCH, Weinheim, 1988.
24. P. Gans, A. Sabatini, A. Vacca, *J. Chem. Soc. Dalton Trans.,* 1195 (1985)
25. L.-Olof Öhman, W. Forsling, *Acta Chem. Scand.,* **A35** (1981) 795-802
26. T. Hedlund, S. Sjöberg, L.-Olof Öhman, *Acta Chem. Scand.,* **A41** (1987) 197-207.
27. V. A. Nazarenko, E. M. Nevskaya, *Russ. J. Inorg. Chem.,* **14** (1969) 1696.
28. D. Attwood, A. T. Florence, *Surfactant Systems,* Chapman and Hall, London, 1983; K. L. Mittal (ed.), *Micellization, Solubilization and Microemulsions*, Plenum Press, N.Y., 1977; Internet WEB, http://www.surfactants.net
29. G. Berthon, *Coord. Chem. Rev.,* **149** (1996) 241-280
30. L. A. Kul'skii, V. F. Nakortschevskaya, *Khimiya vody (Chemistry of Water)*, Vischa schola, Kiev, 1983.
31. P. R. Danesi, R. Chiarizia, G. Scibona, R. Riccardi, *Inorg. Chem.,* **12** (1973) 2089-2091
32. L. D. Pettit (University of Leeds, U.K.), private communication

**Received: December 17, 1999 - Accepted: January 10, 2000 -
Accepted in publishable format: June 14, 2000**