Dependence on Ionic Strength of Stability Constants, Protonation and Complexation of 2,X-dihydroxybenzoic Acids(X = 4, 5 or 6) with Aluminium(III)

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CONTENTS

A. ABSTRACT

The complexation of aluminium(III) with 2,X(X = 4, 5, 6)-dihydrobenzoic acids (DHBA) has been investigated potentiometrically. The temperature was kept constant at 25 °C and the ionic strengths were kept (0.1, 0.3, 0.5, 0.7 and 0.9) mol/1 in sodium chloride media. It was shown that aluminium(III) form a mononuclear $Al(HL)^+$ type 1:1 complex with 2,X(-DHBA), where L^{3-} represents the fully dissociated 2,X(X = 4, 5, 6) anion at pH = 4 - 5. The stochiometries of the complexes were determined by continuous varitions method. The protonation constants of 2,X(-DHBA) (using the potentiometric technique) and the stability constant of the complex were determined at different ionic strengths. The dependence of ionic strength on the protonation and stability constants was evaluated using a simple Debye - Huckel type equation.

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B. INTRODUCTION

The aqua aluminium(III) ion is the hardest of the trivalent ions commonly found in biological systems and in the environment. Its effective ionic radius of 0.54 Å is considerably smaller than other commonly encountered trivalent metal ions /1/. Because of its small ionic radius, the Al(III) ion has a strong tendency to undergo complex hydrolytic reactions, and consequently quantitative studies of its reactions in aqueous solution have lagged far behind those of most other common divalent and trivalent metal ions. It is, therefore, not surprising that, except for a few phenolic and multidentate polyamino polycarboxylic acids, quantitative studies of aluminium(III) complexes have been carried out only at low pH($\leq$3), where hydrolytic species are generally absent /2/.

Although aluminium was previously regarded as a relatively innocuous element, it has recently been found that certain aquatic forms appear to be a very serious threat to aquatic life. However, it has also been found that although the Al(III) ion and hydrolytic complexes thereof predominantly cause fish death and root damage at low concentrations, the toxic effects greatly diminish if the metal ion is bound to an organic ligand or to an inorganic ligand other than the hydroxide ion. Today, it is believed that aluminium plays a toxic role in several human diseases and disorders /3/.

Several authors carried out studies on aluminum speciations /1,3-9/; some of them were interested in speciation particularly in biological fluids. Desroches *et al.* /8/ especially investigated Al(III) complex equilibria with two catechol derivatives, two pyridones, including desferrioxamine-B(desferol, DFO), in order to substitute to DFO in the clinical treatment of aluminum intoxication. Kiss *et al.* /7/. reviewed the studies related with the solution states of Al(III) in organism and the biospeciation of Al(III) ion in its transport.

We have already determined the stability constants of the complexes formed between Al(III) and some catechol derivatives /4/. We were also interested in the protonation constants (log K) of hydroxybenzoic acids,(H₃L), (2,X-dihydroxybenzoic acids, 2,X-DHBA, X=4,5 or 6), which contain additional phenolate besides salicylate sites /10/.

Kiss and coworkers determined the protonation constants of various bi-, tri- and tetradentate catechol and salicylic acid derivatives and the stability constants (log β) of their Al(III) complexes /5/. Although they accepted the speciation model proposed by Öhman *et al.* /11/ for the aluminum(III)-salicylate(SA) system; their corresponding stability constants of the binary and ternary complexes of the same system were not in agreement with the results of Öhman *et al.* /11/. Besides these discrepancies, Kiss *et al.* /5/ have not rigorously checked thermodynamic equilibrium in the potentiometric titrations reported in the corresponding data base of Al(III)-(2,X-DHBA) systems. It is worthwhile to note that the reliability of a given simulation model crucially depends on that of the parameters fed into the corresponding data base /6/. When the experimental conditions of Kiss *et al.* /5/ are evaluated it is noticed that the reported results of Al(III)-2,X-

DHBA systems were found from pH values read in 1-3 minutes. But they have investigated the coordination abilities of Al(III) with several ligands in the last decade /12-14/. They rigorously controlled thermodynamic equilibrium and selected the data for computer evaluation, especially describing in detail pH-potentiometric solution speciation measurements of bioactive complexes and different Al(III)-ligand systems /7, 12-14/.

Due to the rather sluggish ligand-exchange kinetics of Al(III), Kiss *et al.* /14/ applied a strict criterion; when equilibration could not be reached in 10 minutes, the corresponding titration points were omitted from the calculations.

Considerable studies have been performed on the ionic strength dependence of the stability constants of some weak complexes of alkali and alkaline earth metals with some organic and inorganic ligands, /15-20/, and little work has been carried out for more stable complexes of α-amino acids with transition metal ions /21-24/, but according to the literature no work has been reported on the ionic strength dependence of stability constants, protonation and complexation of aluminium(III) with 2,X-dihydroxybenzoic acids (2,X-DHBA, X=4,5 or 6).

The present work deals with the study of Al(III): 2,X(X = 4, 5, 6)DHBA system in an ionic strength range 0.1 - 0.9 mol/L sodium chloride. The parameters which define this dependency were analyzed with the aim of obtaining further insight into their variation as a function of charges involved in the complex reaction. Moreover, general equations were established for the dependence of protonation and stability constants on ionic strength. These equations give the possibility of estimating a protonation constant and a stability constant at a fixed ionic strength when its value is known at another ionic medium in the range $0.1 \leq I \leq 0.9$ M. and therefore may make a significant contribution to solving many analytical and speciation problems.

C. EXPERIMENTAL

1. Materials.

All the chemicals were of analytical-reagent grade and were used as received. All solutions were made with bi-distilled, deionized and CO_2-free water. 2,4-DHBA was purchased from Fluka and 2,5-DHBA with 2,6-DHBA were purchased from Aldrich. The purities of these ligands were periodically checked by Gran method /25/. The aluminum stock solution (0.01 M) was prepared by dissolving $AlCl_3.6H_2O$ (99 %, Merck) in a small excess of HCl (Merck, 37%, d=1.18) in order to avoid hydrolysis, and it was standardized by back titration with EDTA /26/. The concentration of free acid in the Al(III) solution was systematically checked, by potentiometric titration, before each series of experiments. 0.1 M sodium hydroxide(Merck, proanalyse) solution was prepared as carbonate-free solution and was standardized against potassium hydrogen phthalate (99.9%, Merck). Sodium chloride (Merck, proanalyse) was the supporting electrolyte to maintain constant activity coefficients and to obtain the stability constants to be used in computer simulation models referring to blood plasma.

2. Potentiometric measurements.

pH-metric measurements of 50.0 cm^3 samples were carried out under an inert atmosphere of water-NaOH saturated nitrogen in a water-jacketed vessel maintained at 25°C ± 0.1 °C. The ionic strenght was maintained from 0.1 to 0.9 mol/L with NaCl. Four potentiometric titrations were carried out for each ligand studied; the first one was performed with the ligand alone to determine its protonation constant; the others took place in the presence of ligand and Al(III) ion. Al(III) to ligand ratios were 1:1, 1:2, 1:3 and 1:10. The titrations were performed within the limits 2≤pH≤10, except 1:1 mole ratio; a waiting time of at least 10± 2 minute was taken before pH readings to reach thermodynamic equilibrium in 1:1 mole ratio: When equilibration could not be reached the titration was ended, since drifts on pH values started due to the precipitation reactions. But the time necessary for thermodynamic equilibrium in 1:2, 1:3, 1:10 mole ratios was around 4 ± 2 minutes. pH-metric titrations were performed with Schott automatic piston burette to deliver the titrant. NaOH standard, and the pH values were directly measured with a Schott model pH meter (Hofheim-Germany), fitted with a combined electrode. The electrode system was calibrated for hydrogen ion concentration according to Irving *et al.* /27/ The corresponding logarithmic values of the ionic product of water were determined to be 13.71, 13.66, 13.65, 13.65 and 13.69 at the ionic strengths 0.1, 0.3, 0.5, 0.7 and 0.9, under the present conditions. In the calibration step of the pH meter the pH reproducibility is < 0.005 units in acidic pH region and < 0.015 units in basic pH region. The same procedure was performed for the other ionic strengths.

3. Spectroscopic measurements.

The stoichiometries of the formed complexes were defined by spectroscopy. The pH dependent changes in absorbances of the ligands were correlated from the potentiometric titration curves of the ligands alone. The maximum absorbances were observed at defined pH values (their pH values were 4.0 – 5.0); so that they were λ=315 nm for 2,4-DHBA, λ=350 nm for 2,5-DHBA and λ=340 nm for 2,6-DHBA.

The most appropriate working wavelength for the Al(III):2,4-DHBA system was defined at pH=4.1, λ=315 nm, for the Al(III):2,5-DHBA system at pH=4.2, λ=350 nm and for the Al(III):2,6-DHBA system at pH=4.0, λ=340 nm.

The spectra of the Al(III):2,4-DHBA systems were taken at pH=4.1 in order to define the absorbances of the species which exist at λ=315 nm in 1:1 Al(III):2,4-DHBA system (Fig. 1).

Job's plots /28/ were drawn for each Al(III): 2,X(X = 4, 5 or 6)DHBA system at those working wavelengths and then the stoichiometries of the complexes were defined from Job's plots (Fig. 2, it is given only for the Al(III):2,4-DHBA system). The stoichiometry of the formed complexes (with the above-mentioned ligands) corresponds to X=0.5, meaning that only the $Al(HL)^+$ type complex exists at pH=4.0 – 4.2 for 1:1 mole ratios.
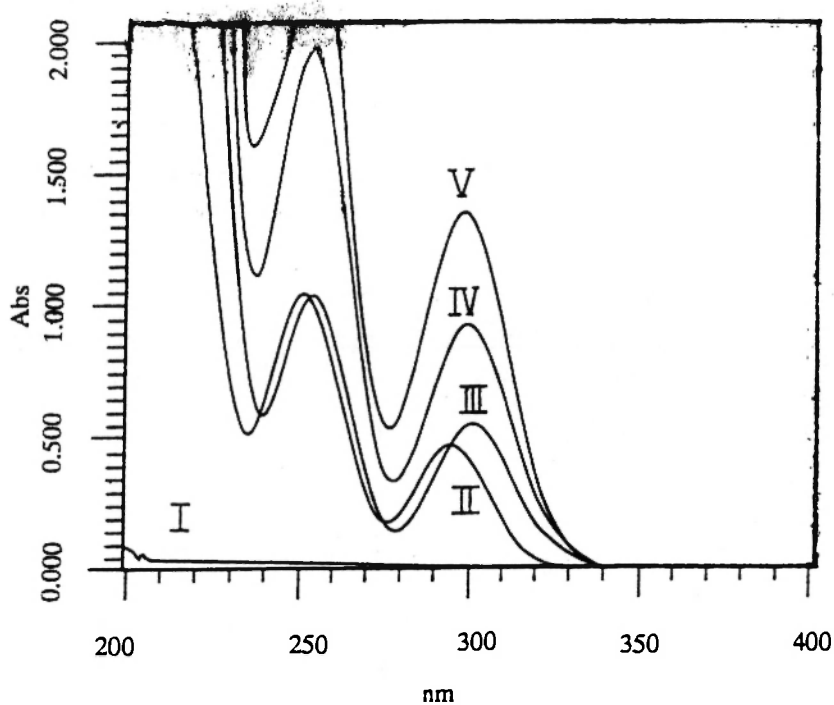
Fig. 1: Absorption spectra of Al(III) complex of 2,4-DHBA in 0.1 M NaCl at 25°C (pH=4.1)

    I.   Al(III) alone ($T_{Al}= 1 \times 10^{-4}$M).

    II. 2,4-DHBA alone ($T_L = 1 \times 10^{-4}$M).

    III. (1:1) Al(III)-2,4-DHBA ($T_{Al} = 1 \times 10^{-4}$ M, $T_L = 1 \times 10^{-4}$M).

    IV. (1:2) Al(III)-2,4-DHBA($T_{Al} = 1 \times 10^{-4}$M, $T_L = 2 \times 10^{-4}$M).

    V. (1:3) Al(III)-2,4-DHBA($T_{Al} = 1 \times 10^{-4}$M, $T_L = 3 \times 10^{-4}$ M).
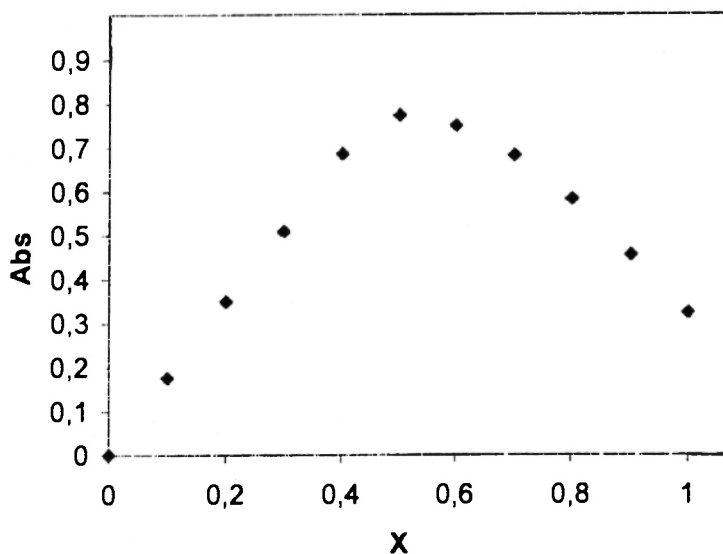

**Fig. 2:** Job's plot for Al(III)-2,4-DHBA in pH=4.1 at λ=315 nm

4. Calculations.

All the calculations were performed with the micro computer program BEST /29/. The BEST program calculation begins with the set of known and unknown (estimated) overall stability constants and computes [H] at the equilibrium for each quantity of added base. For each equilibrium point, the fitting process consists in the minimization of the differences between the observed and the calculated $p[H^+]$ values by using a weighted least square method. The literature process is repeated until no further minimization is obtained. All other mathematical aspects are described elsewhere /30-32/.

In order to apply the program to each Al(III) 2,X-DHBA(X = 4, 5 or 6) system, 99 experimental points of titration were introduced into BEST in each case. Thus the mathematical analysis of the data comprising 12 titrations was performed and the averages of constants obtained from the program are listed in Table1.
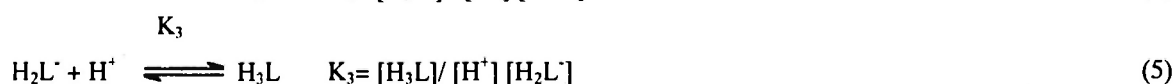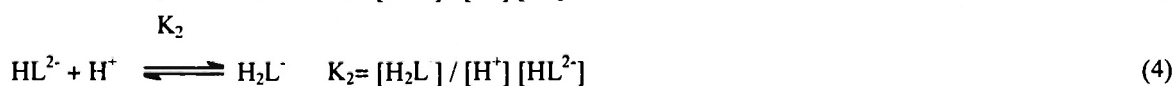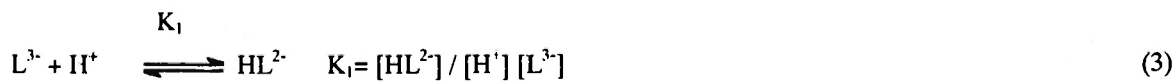
D. RESULTS AND DISCUSSION

The complex $M_xH_yL_z$ $^{(mx+y-nz)+}$ formed is characterized by its stoichiometry (x, y, z), where M and L represent the metal ion and the ligand, respectively. To determine the stability constant of the complexation or the protonation Eq.(1) is defined by β_{xyz} /33/.

$$XM^{M+} + YH^+ + ZL^{N-} \rightleftharpoons M_XH_YL_Z{}^{(MX+Y-NZ)+} \tag{1}$$
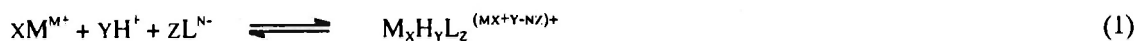
$$\beta_{XYZ} = [M_XH_YL_Z{}^{(MX+Y-NZ)+}] / [M^{M+}]^X[H^+]^Y[L^{N-}]^Z \tag{2}$$

The protonation constants of 2,X-DHBA(X = 4, 5 or 6) have been used for computation of the stability constant of the metal complex (β_{xyz}).

The protonation equilibria of 2,X-DHBA(X = 4, 5 or 6) have been studied in different kinds of background electrolytes, but there are no reports about the ionic strength dependence of the protonation constants of 2,X-DHBA(X = 4, 5 or 6). The following equilibria were studied.

$$L^{3-} + H^+ \xrightleftharpoons{K_1} HL^{2-} \qquad K_1 = [HL^{2-}] / [H^+] [L^{3-}] \tag{3}$$

$$HL^{2-} + H^+ \xrightleftharpoons{K_2} H_2L^- \qquad K_2 = [H_2L] / [H^+] [HL^{2-}] \tag{4}$$

$$H_2L^- + H^+ \xrightleftharpoons{K_3} H_3L \qquad K_3 = [H_3L] / [H^+] [H_2L^-] \tag{5}$$

where L^{3-} represents the fully dissociated 2,X-DHBA(X=4, 5 or 6) anion. The protonation constants K_1, K_2 and K_3 have been determined using potentiometric techniques and calculated using BEST computer program. 2,X-DHBA(X = 4, 5 or 6) ligands have three dissociable protons, but the OH group *ortho* to COO⁻ ion cannot be titrated until pH~13.0, since there is very strong hydrogen bonding between the COO⁻ and OH groups.

Table 1

Protonation Constants of 2,4-DHBA, 2,5-DHBA and 2,6-DHBA

Equilibria Constant Equations	I, mol/L	Protonation Constants (logK)		
		2,4-DHBA	2,5-DHBA	2,6-DHBA
$[HL^{2-}]/[L^{3-}][H^+]$		13.37 ± 0.03 14 /40/	13.74 ± 0.02 14 /40/	13.28 ± 0.04 14 /40/
$[H_2L^-]/[HL^{2-}][H^+]$	0.1	8.95 ± 0.02 8.80 ± 0.01 /40/	10.14 ± 0.03 10.18 ± 0.02/40/	10.39 ± 0.02 11.03 ± 0.04 /40/
$[H_3L]/[H_2L][H^+]$		3.56 ± 0.02 3.16 ± 0.01 /40/	2.85 ± 0.01 2.79 ± 0.01 /40/	1.25 ± 0.05 1.20 ± 0.06 /40/
$[HL^2]/[L^3][H^+]$		14 ± 0.03	13.97 ± 0.09	13.90 ± 0.1
$[H_2L^-]/[HL^{2-}][H^+]$	0.3	8.76 ± 0.03	10.45 ± 0.06	11.17 ± 0.03
$[H_3L]/[H_2L][H^+]$		2.98 ± 0.03	2.91 ± 0.06	± 0.05
$[HL^{2-}]/[L^{3-}][H^+]$		12.82 ± 0.05 1.373 ± 0.002	11.55 ± 0.02 12.74 ± 0.02 /40/	14.00 ± 0.5 13.283 ± 0.02 /40/
$[H_2L^-]/[HL^{2-}][H^+]$	0.5	8.64 ± 0.05 8.555 ± 0.002	10.06 ± 0.03 9.995 ± 0.004 /40/	11.10 ± 0.2 12.571 ± 0.002 /40/
$[H_3L]/[H_2L^-][H^+]$		3.13 ± 0.05 3.118 ± 0.002	2.79 ± 0.03 2.731 ± 0.002 /40/	0.95 ± 0.1 1.196 ± 0.002 /40/
$[HL^{2-}]/[L^{3-}][H^+]$		12.26 ± 0.02	11.51 ± 0.03	13.99 ± 0.4
$[H_2L^-]/[HL^{2-}][H^+]$	0.7	8.55 ± 0.02	9.97 ± 0.03	11.00 ± 0.5
$[H_3L]/[H_2L][H^+]$		2.96 ± 0.02	2.64 ± 0.03	0.89 ± 0.2
$[HL^2]/[L^3][H^+]$		13.75 ± 0.06	12.93 ± 0.07	14.00 ± 0.6
$[H_2L^-]/[HL^{2-}][H^+]$	0.9	8.55 ± 0.06	10.08 ± 0.07	11.22 ± 0.03
$[H_3L]/[H_2L][H^+]$		3.05 ± 0.06	2.68 ± 0.07	0.96 ± 0.05

Therefore only one inflection at m=1.0, where m is moles of base per mole of H_3L ligand, was observed in the potentiometric titrations of 2,X-DHBA(X = 4, 5 or 6) ligands (Fig.3-curve I, for simplicity only the potentiometric titration curve of 2,4-DHBA is given). The protonation constants logK are in good agreement with those reported previously, /5, 34, 35/, especially if the differences between experimental conditions are taken into account. These values are listed in Table 1 together with the values reported in the literature.
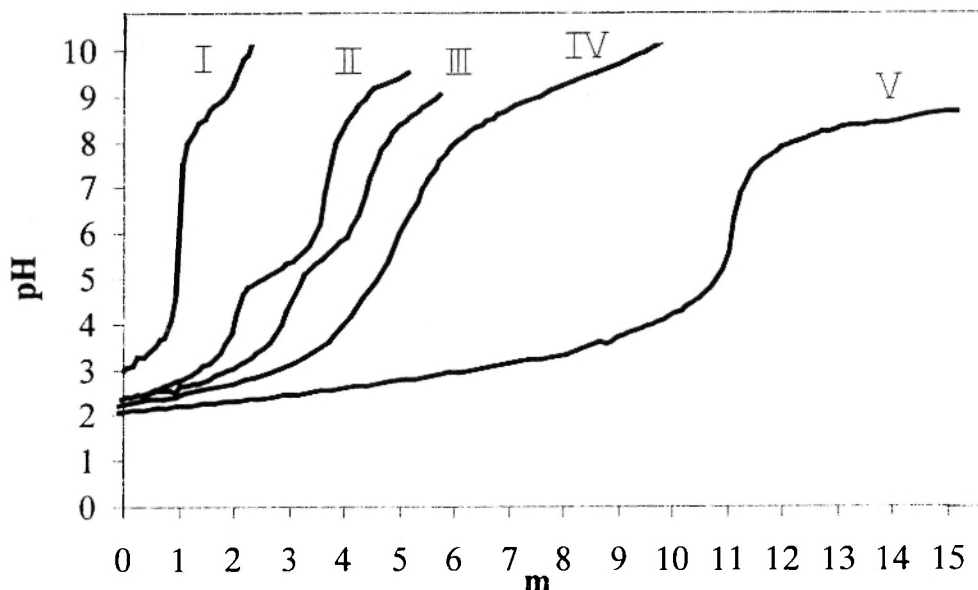

Fig. 3: Potentiometric titration curves of Al(III) complexes of 2,4-DHBA in 0.1 M NaCl at 25°C ± 0.1 °C.

I.   2,4-DHBA alone (T_L= 9.6×10^{-3} M)

II. (1:1) Al(III): 2,4-DHBA (T_{Al}= 9.6×10^{-3} M, T_L= 9.6×10^{-3} M).

III. (1:2) Al(III): 2,4-DHBA (T_{Al}= 9.6×10^{-3} M. T_L= $19,2 \times 10^{-3}$ M).

IV. (1:3) Al(III): 2,4-DHBA (T_{Al}= 9.6×10^{-3} M, T_L= $28,8 \times 10^{-3}$ M).

V.   (1:10) Al(III): 2,4-DHBA (T_{Al}= 9.6×10^{-3} M, T_L= 9.6×10^{-2} M).

.Al(III) complexes with 2,4-DHBA, 2,5-DHBA and 2,6-DHBA were observed. Titration of a 1:1 molar ratio of 2,X-DHBA(X = 4, 5 or 6) to Al (III) ion resulted in a sloping buffer region and a steep inflection at m=2.0 (where m is the moles of base per moles of Al(III), only for one concentration and for Al(III)-2,X-DHBA(X = 4, 5 or 6) system are titration curves (as given in Figure 3) indicating the stability of a chelate type of Al(HL)' (between m=0.0 and m=2.0). Again a steep inflection was observed at m=3.0 and hydrolysis of Al(HL)' complex ion (Fig.3 , curve II).

The potentiometric titration curves of Al(III)-2,X-DHBA(X = 4, 5 or 6) systems in 1:2 and 1:3 mole ratios showed only one inflection at m=3.0 and m=4.0, respectively. However. since no precipitation was noticed when the limits of titrations were 2< pH ≤10 and the range of mole ratios was 1:2 and 1:3 mole ratios, this can be fully explained assuming that the coordination of only one mole of 2,X-DHBA(X = 4, 5 or 6) to Al(III) occurs, and therefore the titration of uncoordinated one and two moles of 2,X-DHBA(X = 4, 5 or 6) ligands were carried out for 1:2, and 1:3 mole ratios, respectively. As a result the occurrence of only mononuclear species Al(HL)' can be proposed (Fig. 3 , curves III and IV).

Titration of a solution with 1:10 molar ratio of metal ion to ligand resulted in a greater depression of the first buffer region (m=0.0–11.0), corresponding to more complete stability of the 1:1 chelate (two moles of proton lost from one of 2,X-DHBA(X = 4, 5 or 6) and 9 protons lost from 9 moles of 2,X-DHBA(X = 4, 5 or 6) protons) (Fig. 3, curve V).

The concentrations of all assumed species were calculated from related equations and then drawn as a function of $-\log [H^+]$ (Fig. 4)
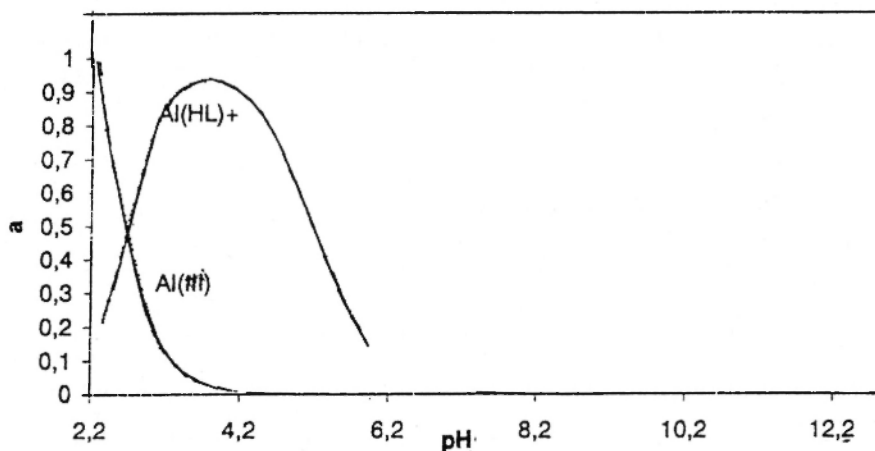

Fig. 4: Species distribution curves of the Al(III) ion and 2,4-DHBA system as a function of $-\log [H^+]$.(a:mole fraction)

The speciation curves show that the major speciation in the defined pH range are Al(III) ion and Al(HL)$^+$ complex ion, in which 2,4-DHBA acts as a bidentate ligand. The occurrence of the salicylate (COO$^-$, O$^-$) bonding mode was confirmed by the speciation curves.

The dependence on ionic strengths of protonation and stability constants can be described by general equations, $\log\beta_{xyz} = f(I)$, which can be used for all the protonation and stability constants if allowance is made for the stoichiometry and for the charges involved in the reaction. The semi-empirical Debye – Hückel type equation, Eq. (6), can be used for taking into account the dependence of $\log\beta_{xyz}$ on I for each complex species /15-24, 36-38/.

$$\begin{aligned}\log\beta_{xy}(I) = \log\beta_{xy}(I') &- Az^*[\, I^{1/2}/(1 + BI^{1/2}) - I'^{1/2}/(1 + BI'^{1/2})] \\ &+ C(I - I') + D(I^{3/2} - I'^{3/2}) + E(I^2 - I'^2),\end{aligned} \tag{6}$$

where I and I′ are the actual and reference ionic strengths, $z^* = \Sigma(\text{charges})^2\text{reactants} - \Sigma(\text{charges})^2\text{products}$, A and B are the parameters of the Debye – Hückel equation. Considering

$$A = 0.5115 + 8.885\times10^{-4}(t - 25) + 2.953\times10^{-6}(t - 25)^2 \tag{7}$$

$$B = 1.489 + 8.772\times10^{-4}(t - 25) + 4.693\times10^{-6}(t - 25)^2, \tag{8}$$

where t is the temperature in degrees Celsius.

Eq. (6) can be simplified at $t = 25\ °C$ as

$$\log\beta_{xyz}(I) = \log\beta_{xyz}(I') - z^*[\,I^{1/2}/(2 + 3I^{1/2}) - I'^{1/2}/(2 + 3I'^{1/2})\,] + C(I - I')$$
$$,+ D(\,1^{3/2} - I'^{\,3/2}\,) + E(\,I^2 - I'^2\,) \tag{9}$$

where C, D and E are empirical parameters which can be obtained by a regression method with a suitable computer program and are reported in Table 2. $D(\,I^{3/2} - I'^{\,3/2}\,)$ or $E(\,I^2 - I'^2\,)$ very often improves the fit of the data. For example, for protonation constant of the OH group in position 4 of 2,4-DHBA, from Eq. (9), we obtained three sets of values depending on whether or not we take into account the term in D and E:

C = − 0.095, D = 0.0,   E = 0.0, U = 0.002

C = − 0.371, D = 0.290, E = 0.0, U = 0.001

C = −1.740, D = − 4.307, E = 2.627, U = 1.07x10^{-4}

Table 2

Parameters for the Dependence on Ionic Strength of Protonations and Al(HL)$^+$

Species		C	D	E	z*	U
2,4-DHBA	K_1	88.380	− 193.948	112.083	6	0.001
	K_2	1.740	− 4.307	2.627	4	1.07x10^{-4}
	K_3	− 13.775	25.060	− 12.431	2	0.030
2,5-DHBA	K_1	94.924	− 219.805	130.742	6	0.300
	K_2	24.482	− 49.998	27.292	4	0.009
	K_3	9.463	− 19.426	10.507	2	4.78x10^{-4}
2,6-DHBA	K_1	19.774	− 32.194	14.880	6	2.38x10^{-4}
	K_2	32.682	− 61.239	31.740	4	1.44x10^{-4}
	K_3	3.011	− 8.209	5.285	2	3.92x10^{-6}
Al(III):2,4-DHBA	β_{111}	− 10.800	30.860	− 19.967	12	0.006
Al(III):2,5-DHBA	β_{111}	20.965	− 37.470	19.133	12	8.1x10^{-5}
Al(III):2,6-DHBA	β_{111}	− 40.658	82.546	− 44.973	12	0.099

The squares sum, U, shows that there is a significant improvement in the fit when D and E terms are introduced. We used the Gauss − Newton nonlinear least-squares method in the computer program /39/ to refine the parameters C, D and E by minimizing the squares sum from Eq. (10)

$$U = \Sigma\,(a_i - b_i)^2 \quad (i = 1, 2, 3, ...) \tag{10}$$

where a is a quasi experimental quantity and b is a calculated one.

Using the above values of C, D and E, from Table 2, one can rewrite Eq.(9) for K_1, K_2, K_3 and β_{xy}, as:

2,4-DHBA

$\log K_1(I) = 10.1878 - (\sqrt{I}/(0.333 + 0.5\sqrt{I})) + 88.38\,I - 193.948\,I^{3/2} + 112.083\,I^2$

$\log K_2(I) = 9,3145 - (\sqrt{I}/(0.5 + 0.75\sqrt{I})) + 1.74\,I - 4.307\,I^{3/2} + 2.627\,I^2$

$\log K_3(I) = 4.4838 - (\sqrt{I}/(1 + 1.5\sqrt{I})) + 13.775\,I - 25.06\,I^{3/2} + 12.431\,I^2$

2,5-DHBA

$\log K_1(I) = 10.5349 - (\sqrt{I}/(0.333 + 0.5\sqrt{I})) + 94.924\,I - 219.805\,I^{3/2} - 130.742\,I^2$

$\log K_2(I) = 9.4289 - (\sqrt{I}/(0.5 + 0.75\sqrt{I})) + 24.482\,I - 49.998\,I^{3/2} - 27.292\,I^2$

$\log K_3(I) = 2.6273 - (\sqrt{I}/(1 + 1.5\sqrt{I})) + 9.463\,I - 19.426\,I^{3/2} - 10.507\,I^2$

2,6-DHBA

$\log K_1(I) = 12.8153 - (\sqrt{I}/(0.333 + 0.5\sqrt{I})) + 19.774\,I - 32.194\,I^{3/2} + 14.88\,I^2$

$\log K_2(I) = 9.1699 - (\sqrt{I}/(0.5 + 0.75\sqrt{I})) + 32.682\,I - 61.239\,I^{3/2} + 31.74\,I^2$

$\log K_3(I) = 1.3701 - (\sqrt{I}/(1 + 1.5\sqrt{I})) + 3.011\,I - 8.209\,I^{3/2} + 5.285\,I^2$

Al(III):2,4-DHBA

$\log \beta(I) = 10.2642 - (\sqrt{I}/(0.166 + 0.25\sqrt{I})) - 10.8\,I + 30.86\,I^{3/2} - 19.967\,I^2$

Al(III):2,5-DHBA

$\log \beta(I) = 9.4275 - (\sqrt{I}/(0.166 + 0.25\sqrt{I})) + 20.965\,I - 37.47\,I^{3/2} + 19.133\,I^2$

Al(III):2,6-DHBA

$\log \beta(I) = 14.0656 - (\sqrt{I}/(0.166 + 0.25\sqrt{I})) - 40.658\,I + 82.546\,I^{3/2} - 44.973\,I^2,$

giving protonation and stability constants of 2,X-DHBA and its complex by aluminium(III) at each ionic strength in the range of $0.1 \leq I \leq 0.9$ (Table 3).

The dependences on ionic strength of $\log \beta_{111}$ are shown in Figure 5. Figure 5 shows that the stability constant of Al(III):2,4-DHBA system has a larger value at $I = 0.7$ and a minimum at $I = 0.9$, the stability constant of Al(III):2,5-DHBA system has a larger value at $I = 0.9$ and a minimum at $I = 0.3$ and the stability constant of Al(III):2,6-DHBA system has a larger value at $I = 0.1$ a minimum at $I = 0.9$.

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Table 3

Average values of stability constants of Al(III):H₃L(H₃L :2,4-DHBA, 2,5-DHBA
and 2,6-DHBA) at different ionic strengths, I, NaCl

I,mol /L	log β_{111}		
	2,4-DHBA	2,5-DHBA	2,6-DHBA
0.1	8.67 ± 0.01/41/ 8.71 /5/	9.24 ± 0.01/41/ 9.74 /5/	10.87 ± 0.01/41/ 12.79 /5/
0.3	8.52 ± 0.10	9.47 ± 0.06	9.33 ± 0.04
0.5	8.67 ± 0.20	9.39 ± 0.30	9.56 ± 0.68
0.7	8.81± 0.20	9.30 ± 0.25	9.29 ± 0.04
0.9	8.36 ± 0.10	9.45 ± 0.25	9.11 ± 0.15
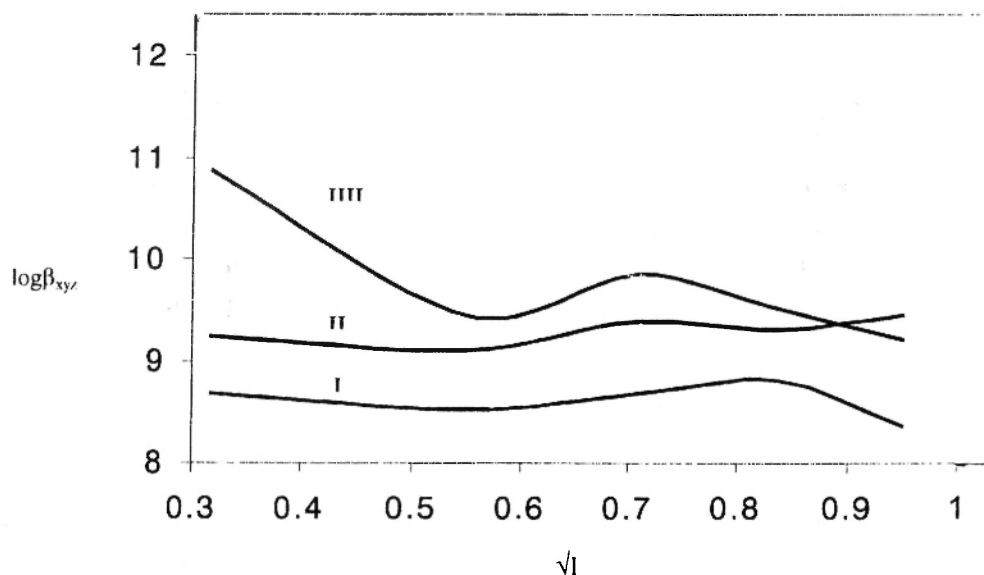
Fig. 5: Plots of (I) logβ₁₁₁ (Al:2,4-DHBA), (II) logβ₁₁₁ (Al:2,5-DHBA) and (III) logβ₁₁₁ (Al:2,6-DHBA) versus the square root of ionic strength.

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