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Potentiometric and Spectroscopic Studies on Aluminium(III) Complexes of Some Catechol Derivatives

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The interactions of aluminium(III) ion with the triprotic catechol derivatives (H_3L), 2,3-dihydroxybenzoic acid (2,3-DHBA), 3,4-dihydroxyphenylacetic acid (3,4-DHPA), 3,4-dihydroxybenzoic acid (3,4-DHBA), and 3,4-dihydroxyhydrocinnamic acid (3,4-DHHCA) were investigated in aqueous solution at 25.0 °C. The Calvin–Bjerrum titration method was adopted for the determination of formation constants of proton–ligand and aluminium(III)–ligand complexes. Potentiometric and spectroscopic results indicated that these catechol derivatives exhibit a true bidentate character. The chelation occurs *via* their catecholate sites, with the exception of 2,3-DHBA. In the case of 2,3-DHBA complexes, the dominant species are either the salicylate type (COO^-, O^-) or catecholate type (O^-, O^-) complex. The protonation constants of ligands and their formation constants of Al(III) complexes were also correlated. The order of decreasing stabilities of complexes is: 3,4-DHPA>3,4-DHBA>3,4-DHHCA>2,3-DHBA.

Key words aluminium; benzoic acid; complex; coordination compound

The aqua Al(III) ion is the "hardest" of the trivalent ions commonly found in the environment and in biological systems. Its effective ionic radius is 54 Å, which is smaller than other commonly encountered trivalent metal ions. Therefore the aqua Al(III) ion has the highest charge/size ratio and high affinity for hard anions. As a result, it has a strong tendency to hydrolyze in aqueous solution and its coordination equilibria contain rather complicated hydroxo complexes.[1,2] The equilibria of aqua Al(III) ions were postulated by Baes and Mesmer[3] including various aluminium-hydroxo species ($\log \beta_n$ values calculated for $I=0.1\,\mathrm{mol \cdot l^{-}}$ in parentheses): $Al(OH)^{2+}$ (−5.461), $Al(OH)_2^+$ (−10.036), $Al_2(OH)_3^{4+}$ (−7.7), $Al(OH)_4^-$, (−23.491), $Al_{13}(OH)_{32}^{7+}$ (−103.149), $Al(OH)_3$ (−13.694), and $Al_3(OH)_4^{5+}$ (−15.737). The formation of Al(III) hydroxo complexes and polynuclear species was also examined and defined by Venturini and Berthon.[4] They showed the existence of $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4^-$, $Al_2(OH)_2^{4+}$, and $Al_3(OH)_4^{5+}$ hydroxo ions.

Alcohols, carboxylic acids, aliphatic monohydroxyacids, aromatic hydroxy acids, and catechol derivatives are typical and effective organic ligands with negative oxygen donors to bind aqua Al(III) ion. Martell *et al.*[2,5] investigated the relations between the basicities of these oxygen donors and the stabilities of their Al(III) complexes. They concluded that the logarithm of protonation constants of monodentate donors and p*K* sum of bi- or terdentate donors provide a quantative measure for the hardness of each donor. The order of decreasing basicities along with the summation of their approximate logarithms of protonation constants are proposed to be: (catecholate *ca.* 22)>(aliphatic monohydroxy acid anion *ca.* 18) >(aromatic hydroxy acid anion *ca.* 16)>(alkoxide *ca.* 14)>(phenoxide *ca.* 10)>(carboxylate *ca.* 4). Therefore the complexes of Al(III) ion that are sufficiently stable to hydrolytic reactions and consequent precipitation in aqueous solution should contain ligands with the highest p*K* sum.

The complexes of catechol derivatives with Al(III) ion including metal ions such as Fe(II), Fe(III), Mg(II), Ca(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Cd(II), UO_2(II), and VO(II) were studied by various researchers.[1,2,5—26] They determined that two or three moles of catechol derivatives are coordinated with one mole of these metal ions in their complexes. In particular, the constants of formation equilibria of Al(III) complexes of catechol derivatives have been the subject of a number of investigations.[1]

Some of the hydroxy aromatic ligands are interesting three-protic ligands (H_3L), 2,3-dihydroxybenzoic acid (2,3-DHBA), 3,4-dihydroxybenzoic acid (3,4-DHBA), 3,4-dihydroxyhydrocinnamic acid (3,4-DHHCA), and 3,4-dihydroxyphenylacetic acid (3,4-DHPA) are typical examples and they have affinities for metal ions to form stable complexes.[19,20,21,26] Some of their complexes do not hydrolyze and precipitate in aqueous solution, since 3,4-DHBA, 3,4-DHHCA, and 3,4-DHPA have one carboxylate binding site besides the catecholate sites that are in chelatable positions. 2,3-DHBA contains three potential binding sites on three adjacent ring carbons. It is a good model of the competitive salicylate (COO^-, O^-) and catecholate type (O^-, O^-) chelation in the same molecule.[5] Kennedy and Powell[7] investigated Al(III): catechol and 3,4-DHBA complexes using potentiometry in aqueous solution in $I=0.1\,\mathrm{mol \cdot l^{-}}$ KCl ionic medium at 25 °C. They reported the stability constants for the mononuclear diphenolate complexes of Al(III) with catechol such as AlL, AlL_2, and AlL_3. They also indicated that mono- and bis- complexes of catechol become hydrolyzed and then $AlL(OH)^-$, and $AlL_2(OH)^{4-}$ hydroxo complexes formed. In the case of 3,4-DHBA, the existence of $Al(HL)^+$, $Al(HL)_2^-$, $Al(HL)_3^{+3}$, Al(OH)(HL), and $Al(OH)(HL)_2^{2-}$ complexes was shown by potentiometric titration. The carboxylate-coordinated $Al(HL)^{2-}$-type complex and the carboxyl-protonated $Al(HL)^+$-type complex were also postulated. To assess the binding ability of Al(III) ion of humic and fulvic acids, which are important organic soil constituents, Kiss *et al.*[14] performed potentiometric studies. The proton and Al(III) complexes of various bi- and terdentate catechol and salicylic acid derivatives (including 3,4-DHBA and 2,3-DHBA) were analyzed and defined at 25 °C at an ionic strength of $0.2\,\mathrm{mol \cdot l^{-}}$ KCl, and the formation constants of AlL- and $Al(HL)^+$-type complexes were determined. In the case of AlL-type chelate, catecholate-type coordination was assumed. Because of the presence of a separate carboxylic

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group in 3,4-DHBA, a mono protonated (1 : 1) $Al(HL)^+$ complex forms in which catecholate-type (O^-, O^-) coordination occurs and the carboxylic group remains protonated. $Al(HL)^+$-type coordination ion has a $-\log K=4.62$ value similar to that of the protonation constant of H_2L^- ion. The same behavior toward 3,4-DHBA was also observed in the corresponding VO(IV) complexes.[26] In addition, Desroches *et al.*[15] reported the Al(III) complex equilibria of five sequestering ligands, including 2,3-DHBA, $Al(HL)^+$, and Al_2L complexes, were characterized for 2,3-DHBA in addition to the species mentioned by Kiss *et al.*[14]

The stability constants of several complexes of substituted catechol ligands including 2,3-DHBA and 3,4-DHPA were examined in acidic solution for Fe(III); evidence were found for the coordination of 3,4-DHPA *via* the carboxylate group which presumably does not involve chelation, while the Fe(III) : 2,3-DHBA system is complicated by mixed-mode coordination of both the catecholate and salicylate type. In the investigation of Cu(II), Zn(II), Ni(II), Cd(II), and Mg(II) complexes with catechol, 3,4-DHBA, and 3,4-DHHCA, the introduction of alkyl groups into the phenol ring decreased their acid strength in the order 3,4-DHBA, 3,4-DHHCA and 3,4-DHPA[19]; the order of the stability constants was in agreement with that of Irving & Williams order (Mn(II) $<$Fe(II)$<$Co(II)$<$Ni(II)$<$Cu(II)$<$Zn(II)). The interaction of 3,4-DHPA with Cu(II) was also investigated by Kiss *et al.*[21] and the ambidentate character of this ligand was observed. In addition to the chelation *via* the catecholate sites, coordination also occurred from a separate carboxylate binding site. The formation of various Cu(II) oligomeric species was also defined.

The first aim of this research was the determination of the formation constants of proton and Al(III) complexes of four different hydroxyaromatic ligands in potentiometric and spectrophotometric studies. Although the complexes of 2,3-DHBA and 3,4-DHBA were investigated by several authors,[14,15] we have included these two ligands in our ligand series to compare the formation constants of their Al(III) complexes with the two other two catechol derivative ligands in the same ionic medium and temperature. Our second aim was the comparison of the basicities of these oxygen donor ligands with the stabilities of their complexes. The third aim was the assignment of the species distribution diagrams for each Al(III) : ligand system to define the conditions to prevent the hydrolysis of aqua Al(III) ion and Al(III) complexes.

Experimental

Materials All the chemicals were of analytical reagent grade. Sodium hydroxide free from carbonate was prepared and standardized with potassium hydrogen phthalate. The stock solutions of Al(III) were prepared by dissolving the appropriate amounts of aluminum chloride (Merck, 99%) in a small excess of HCl,[27] and on indirect titration method was used to standardize this solution.[28] The equivalent points were evaluated using Akalın and Özer's[29] Gran's extrapolation method.[30] 2,3-DHBA was purchased from Sigma, and 3,4-DHBA, 3,4-DHHCA, and 3,4-DHPA were purchased from Aldrich. These ligands were used without further purification. Their molecular weights were periodically checked by Gran titrations.[30] All solutions were prepared in carbon dioxide–free double–distilled water.

Potentiometric Measurements A Schott pH-meter (Hofheim, Germany, accuracy ± 0.05) fitted with a combined electrode was calibrated with acetic acid buffer as well as with standard HCl and NaOH to give hydrogen ion concentrations directly.[31] The Calvin–Bjerrum titration technique was adopted. Measurements were made at 25.0 ± 0.1 °C and the ionic strength was maintained at approximately 0.1 M by the addition of standard KCl solution to Al(III) as a background electrolyte. Purified nitrogen was circulated through the jacketed titration cell under slight pressure to exclude carbon dioxide. All potentiometric titrations were carried out in triplicate. Complexations were investigated within pH intervals, and at least 1—3-min time intervals, were necessary between additions of successive aliquots of sodium hydroxide to reach constant pH.

Spectroscopic Measurements The absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer to measure absorbance and to confirm the existence of deprotonated ligands and complexes at different pH values as a function of wavelength. Job's method was used whenever possible.[32]

Calculations The potentiometric titration curves of four ligands that are catechol derivatives and also are carboxylic acids were compared with their Al(III) : ligand systems (Figs. 1, 2). They were investigated by mathematical analysis of each system. The best complex that accounts for the experimental data was accepted. Nonlinear least-squares analysis of the data in terms of assumed reactions gave a satisfactory fit in the buffer regions of complexes which include Al(III) and one of these ligands in different molar ratios. Then the stochiometries of assumed complexes were deduced from the shapes of titration curves of ligands and Al(III) : ligand systems. The number of potentiometric data for each defined pH region is given in Tables 1 and 2. For computing the protonation constants of ligands[33—35]($\log K$) and the formation constants of Al(III) complexes ($\log \beta$) data were utilized in the pH$=$1.5—3.88 range. The hydrolysis of Al(III) ion was completely neglected in this pH range, but above pH 4.0 the existence of hydroxo complexes was considered. $\log K$, $\log \beta$, and standard derivations of these values that are given in Tables 1 and 2 were obtained from related equations using, the RANA computer program described previously.[32] To determine the stoichiometries of possible complexes, the degree of formation of Al(III) chelates $\bar{n}$ was calculated from the formation curves employing the method of Irving and Rossotti.[35—38] The species distribution diagrams[39] of the Al(III) complexes formed with the above-mentioned ligands at metal-to-ligand molar ratios of 1 : 1, 1 : 2 and 1 : 3 as a function of pH are presented in Figs. 3 and 4.

Results and Discussion

Proton Complexes of Catecholate Derivatives In this research, only two protonation constants of each ligand could be determined. Although 2,3-DHBA, 3,4-DHBA, 3,4-DHHCA, and 3,4-DHPA contain three acidic groups, but only two of these acidic groups can lose protons in the measurable pH range due to the formation of intramolecular hydrogen bonds between the $-COO^-$ and –OH groups. Therefore the protonation constant of the second phenolate (L^{3-}), which is in a meta position to COOH in 2,3-DHBA or in an ortho position to –OH in 3,4-DHBA, 3,4-DHHCA, and 3,4-DHPA, can be determined only with uncertainty.[14] Therefore we introduced only these values that were defined in previous investigations.[11,19,25,33] The protonation constant of H_2L^- and HL^{2-} ions were defined by potentiometric titrations that were carried out at three different ligand concentrations (1.0×10^{-3}, 2.02×10^{-3}, 4.04×10^{-3} M) up to pH 11.5 by introducing approximately 220 experimental data for each ligand. The protonation constant of HL^{2-} ion was also measured spectrophotometrically. To compare our results with values reported in the literature the protonation constants of four ligands are listed in Table 1. It was confirmed that $\log K$ values of three ligands that have the –COOH group at position 4 decrease in the order 3,4-DHPA$>$3,4-DHBA$>$3,4-DHHCA.

Aluminium(III) Complexes of Some Catechol Derivatives Due to the differences between the donor group arrangements of the four aromatic hydroxy ligands, first the coordination of 2,3-DHBA to Al(III) is explained, and then the interaction equilibria of Al(III) ion with the other three ligands is discussed.

Al(III) : 2,3-DHBA System. Potentiometric Results

Table 1. Protonation Constants (log *K*) for 2,3-DHBA,3,4-DHPA, 3,4-DHBA and 3,4-DHHCA

Equilibria of proton complexes ($\log K$)		2,3-DHBA	3,4-HHPA	3,4-DHBA	3,4-DHHCA
1	OH ($L^{3-}+H^+ \rightleftarrows HL^{2-}$)				
	OH at 2.position in 2,3-DHBA	13.1[19]	13.7[19]	13.1[11]	12.15[25]
	OH at 3.position in 3,4-DHBA				
2	OH ($HL^{2-}+H^+ \rightleftarrows H_2L^-$)	9.91±0.01[33]	9.52±0.01[33]	8.66±0.01[33]	9.30±0.01[33]
	OH at 3.position in 2,3-DHBA	10.16±0.01[33a]	9.57±0.01[33a]	9.06±0.01[33a]	9.62±0.01[33a]
	OH at 4.position in 3,4-DHPA,	10.11±0.02[a]	9.49±0.02[a]	8.82±0.04[a]	9.64±0.02[a]
	3,4-DHBA and 3,4-DHHCA				
3	COOH ($H_2L^-+H^+ \rightleftarrows H_3L$)	2.74±0.01[33]	4.24±0.01[33]	4.26±0.01[33]	4.36±0.01[33]
		2.68±0.01	4.20±0.01	4.34±0.01	4.40±0.01
4	$\Sigma \log K$	25.89	27.39	26.26	26.19

a) Spectroscopic data.

The potentiometric titrations of the Al(III) : 2,3-DHBA system in 1 : 1 and 1 : 2 molar ratios were performed. The curves exhibit inflection points at $m=2.00$ and $m=4.00$, respectively, where *m* represents the number of moles of base added per mole of Al(III) ion (Fig. 1, curves II, III, IV). The formation of HL^{2-} ion by dissociation of two protons forms 2,3-DHBA in the $m=0.00$—2.00 range and the formation of Al(HL)$^+$- and Al(HL)$_2^-$-type complex ions occurred as proposed by Kiss *et al.*[14] according to equilibria (1) and (2) (Table 2). Remarkable drops in pH values were observed especially in the first buffer regions of the titration curves of 1 : 1 and 1 : 2 Al(III) : 2,3-DHBA systems when compared with the titration curve of 2,3-DHBA alone. Then $\log \beta$ values of Al(HL)$^+$ and Al(HL)$_2^-$ complexes calculated by considering equilibria (3) and (4), respectively. The potentiometric data indicate the existence of Al(HL)$^+$- and Al(HL)$_2^-$-type complexes and they are supported by calculations. The agreement of our values with those in the literature[14,15] is reflected in Table 2. The observed differences between our values and cited values arise from ionic medium and temperature. Thus the assumption of salicylate-type monomeric complexes was sufficient for a fit to the titration curves especially at a lower ligand excess. Kiss *et al.*[14] also assumed the formation of catecholate-type (O^-, O^-) complexes or monohydroxo-salicylate-type (COO^-, O^-, OH^-) complexes. The second inflections were noticed at $m=3.00$ for the 1 : 1 molar ratio and at $m=4.00$ for the 1 : 2 molar ratio. Moreover, continued decreases in pH readings after $m=2.00$ for the 1 : 1 and $m=4.00$ for the 1 : 2 molar ratios (pH 3.88) were observed. Therefore the titration data of either the 1 : 1 or 1 : 2 Al(III) : 2,3-DHBA systems above pH 3.88 could be fitted only by assuming the formation of a mixed hydroxo complex. The shifts in pH values were noted when we waited for 30 min after addition of base (Fig. 1, curves II, III). In addition to the formation of Al(HL)$^+$- and Al(HL)$_2^-$-type complexes, their hydrolysis according to equilibrium (5) between $m=2.00$—3.00 and by equilibrium (6) between $m=4.00$—5.00 was assumed, respectively. Hence these assumptions were supported by calculations (Table 2).

Formation Curve The formation curve, −log ligand concentration *versus* number of ligands bound, $\bar{n}$, was drawn for the Al(III) : 2,3-DHBA system. The $\bar{n}$ values ($1.0<\bar{n}<2.0$) indicate the occurrence of 1 : 1 and 1 : 2 complexes, (Al(HL)$^+$ and Al(HL)$_2^-$), respectively (Fig. 5).

Speciation Diagram The concentrations of all assumed species were calculated from related equations and then drawn as a function of $-\log[H^+]$ (Fig. 3). The speciation curves show that the major species in the defined pH range are Al(III) ion and Al(HL)$^+$, Al(HL)$_2^-$, Al(HL)(OH), and Al(HL)$_2$(OH)$^{2-}$ complexes in which 2,3-DHBA acts as a bidentate ligand. The occurrence of the salicylate (COO^-, O^-) bonding mode was confirmed by the speciation curves.

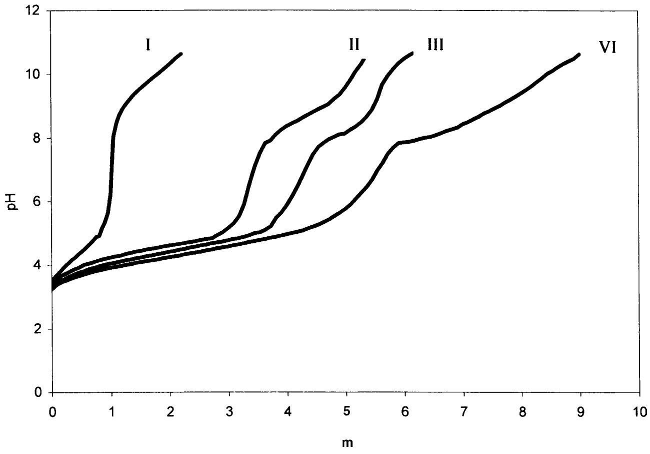

Fig. 1. Potentiometric Titration Curves of Al(III) Chelates of 2,3-DHBA in 0.1 M KCl at 25 °C

I. 2,3-DHBA alone ($T_L=2.02\times10^{-3}$ M). II. (1 : 1) Al(III) : 2,3-DHBA ($T_{Al}=2.02\times10^{-3}$ M, $T_L=2.02\times10^{-3}$ M). III. (1 : 2) Al(III) : 2,3-DHBA ($T_{Al}=2.02\times10^{-3}$ M, $T_L=4.04\times10^{-3}$ M). IV. (1 : 3) Al(III) : 2,3-DHBA ($T_{Al}=2.02\times10^{-3}$ M, $T_L=6.06\times10^{-3}$ M).

Spectroscopic Results The stochiometries of complexes formed were examined based on the spectroscopic results. Job's method was applied by taking the UV/V is spectrum of 2,3-DHBA alone. The pH-dependent change in optical absorption for 2,3-DHBA alone was defined from the potentiometric titration curve. It was noted that the HL^- type ion of 2,3-DHBA occurred at pH 3.08. The occurrence of the Al(HL)$^+$-type complex ion in the pH 2.58—3.83 range was confirmed by taking the spectra of either 2,3-DHBA solution or Al(III) : 2,3-DHBA in a 1 : 1 molar ratio at pH 3.05 (Fig. 6, curves I, II). The maximum absorbance was observed at $\lambda=335$ nm for the 1 : 1 molar ratio; but 2,3-DHBA alone was not absorbed. Job's plots were drawn at $\lambda=335$nm that show maximum absorbance at the molar fraction of Al(III) $X_M=0.5$ for solution in which the pH is 3.05; in other words, the stochiometry of the complex confirms the Al(HL)$^+$-type structure.

Table 2. Equilibrium Constants (log *K*) and formation constants (log β) of Aluminium(III): Catechol Derivatives Chelates at 25 °C, *I*=0.1 M KCl

Equilibrium	2,3-DHBA	3,4-DHPA	3,4-DHBA	3,4-DHHCA
1) $Al^{3+}+H_3L \rightleftarrows Al(HL)^{+}+2H^{+}$	−2.87$^{14)}$ −2.32±0.01			
2) $Al^{3+}+2H_3L \rightleftarrows Al(HL)^{2-}+4H^{+}$	−8.12$^{14)}$ −7.37±0.01	−10.04±0.01	−10.25±0.01	−11.06±0.01
3) $Al^{3+}+HL^{2-} \rightleftarrows Al(HL)^{+}$	10.32$^{14)}$, 10.505$^{15)}$ 10.5±0.05			
4) $Al^{3+}+2HL^{2-} \rightleftarrows Al(HL)_2^{-}$	18.26$^{14)}$, 18.244$^{15)}$ 18.8±0.05			
5) $Al(HL)^{+}+OH^{-} \rightleftarrows Al(HL)(OH)$	9.74±0.002			
6) $Al(HL)_2^{-}+OH^{-} \rightleftarrows Al(HL)_2OH^{2-}$	9.82$^{14)}$ 7.53±0.02			
7) $Al^{3+}+H_3L \rightleftarrows Al(H_2L)^{2+}+H^{+}$		−4.25±0.01	−4.3±0.01	−4.39±0.01
8) $Al\,(H_2L)^{2+} \rightleftarrows AlL+2H^{+}$		−13.26±0.01	−13.04±0.01	−14.55±0.01
9) $Al^{3+}+L^{3-} \rightleftarrows AlL$		17.4±0.05	16.7±0.05, 16.87$^{7)}$, 16.47$^{14)}$, 15.03$^{34)}$	15.9±0.05
10) $AlL+OH^{-} \rightleftarrows AlL(OH)^{-}$		8.87±0.02	7.91±0.02	8.16±0.01
11) $Al(HL)_2^{-} \rightleftarrows AlL_2^{3-}+2H^{+}$		−13.26±0.01	−13.04±0.01	−14.55±0.01
12) $Al^{3+}+2L^{3-} \rightleftarrows AlL_2^{3-}$		28.4±0.05	26.9±0.04, 29.88$^{7)}$, 29.38$^{14)}$, 27.6$^{34)}$	25.8±0.05
13) $AlL_2^{3-}+OH- \rightleftarrows AlL_2(OH)^{4-}$		5.38±0.02	5.3±0.02	5.2±0.012
14) $Al^{3+}+3H_3L \rightleftarrows Al(HL)_3^{3-}+6H^{+}$		−17.34±0.01	−16.92±0.01	−19.41±0.01
15) $Al(HL)_3^{3-} \rightleftarrows AlL_3^{6-}+3H^{+}$			−22.60±0.01	
16) $Al^{+}+3L^{3-} \rightleftarrows AlL_3^{6-}$		38.6±0.05	35.7±0.05, 38.64$^{7)}$, 38.35$^{14)}$, 37.55$^{34)}$	34.6±0.05

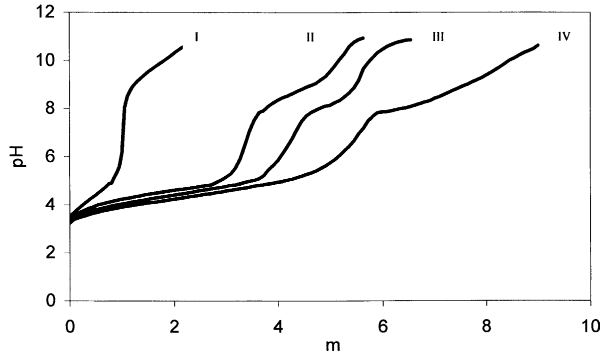

Fig. 2. Potentiometric Titration Curves of Al(III) Chelates of 3,4-DHHCA in 0.1 M KCl at 25 °C

I. 3,4-DHHCA alone (T_L=2.02×10^{-3} M). II. (1 : 1) Al(III) : 3,4-DHHCA (T_{Al}=2.02×10^{-3} M, T_L=2.02×10^{-3} M). III. (1 : 2) Al(III) : 3,4-DHHCA (T_{Al}=2.02×10^{-3} M, T_L=4.04×10^{-3} M). IV. (1 : 3) Al(III) : 3,4-DHHCA (T_{Al}=2.02×10^{-3} M, T_L=6.06×10^{-3} M).

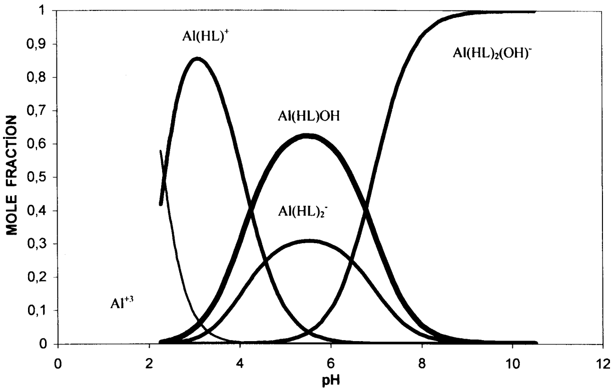

Fig. 3. Species Distribution Curves of the 2,3-DHBA System and the Metal Ion Al(III) as a Function of −log [H^{+}]

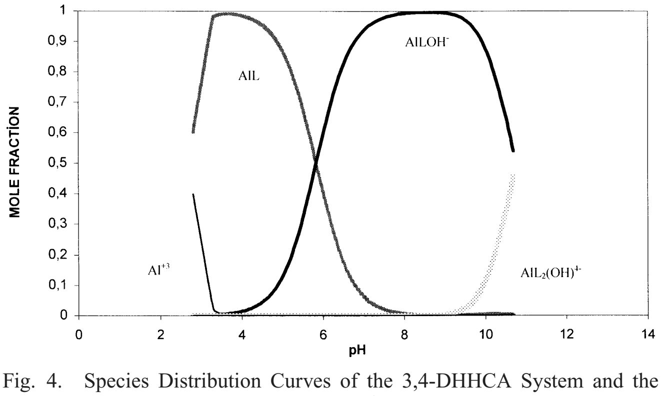

Fig. 4. Species Distribution Curves of the 3,4-DHHCA System and the Metal Ion Al(III) as a Function of −log [H^{+}]

Al(III) : 3,4-DHPA, Al(III) : 3,4-DHBA and Al(III) : 3,4-DHHCA Systems. Potentiometric Results The potentiometric titrations were performed in 1 : 1, 1 : 2 and 1 : 3 molar ratios of Al(III) : ligand systems in 0.1 mol · l^{-} KCl ionic medium at 25 °C. The series of titration curves are given only for the Al(III) : 3,4-DHHCA system since they are similar in each system. In 1 : 1 molar ratios of Al(III) : ligand systems, the first inflection points on potentiometric titration curves were observed at *m*=4.00 The potentiometric titration curves of 3,4-DHHCA alone and the Al(III) : 3,4-DHHCA system clearly indicate that in *m*=0.00—1.00 range equilibrium (7) (in Table 2) occurs (Fig. 2, curve II). It was verified that in the *m*=0.00—1.00 range a proton from the uncoordinated carboxyl was titrated; the protonation constants of H_2L^{-} ion for these three ligands are equal to the assumed formation constants of $Al(H_2L)^{+2}$-type ions (Table 1). Then the coordination of ligand to Al(III) ion from two phenolate oxygens that are in the 3 and 4 positions to the carboxyl was considered in *m*=1.00—3.00 range [Table 2, equilibrium (8)]. Thus deprotonations of two phenolic hydroxyl groups and the formation of an AlL-type complex according to equilibrium (9) were assumed. log *K* values for equilibria (7) and (8) were determined, and then the formation constants (log β) for AlL in the pH range for the Al(III) : 3,4-DHPA system, in the pH range of 3.77—4.90 for the Al(III) : 3,4-DHBA system, and in the pH range of 4.29—4.86 for the Al(III) : 3,4-DHHCA system (Fig. 2, curve II) were calculated by introducing approximately 76 experimental data for each Al(III) : ligand system (Table 2). Thus the occurrences of AlL-type complexes that have a catecholate mode of coordination were supported by potentiometry. In addition to the $\log\beta$ value for 3,4-DHBA that was determined by Hancock and Orszulik,[34)] other $\log\beta$ values[7,14)] are in a comparable range with our value. The shifts in pH values beyond pH *ca.* 4.80 in all Al(III) : ligand systems might be attributed to the hydrolytic equilibrium (10) that was proposed in the $m=3.00$—4.00 range. The occurrence of hydroxo complex formation was confirmed by calculation of the equilibrium constant (Table 2, row 10). In the case of the 1 : 2 molar ratio of Al(III) : ligand systems, the inflection points of potentiometric titration curves were observed at $m=5.00$ and $m=7.00$ (Fig. 2, curve III). The stepwise coordination of two moles of ligands to Al(III) were assumed according equilibria (2) and (11) in the $m=0.00$—4.00 range (pH 3.48—5.27). Thus the equilibrium constant of (2) was confirmed; as a result, the constant of equilibrium (4) was calculated by introducing 118 experimental points. Hence the occurrence of salicylate (type coordination (COO^-, O^-) and the formation of an $Al(HL)_2^+$ (type complex were confirmed in the $m=0.00$—4.00 range. However, after that the coordination sites change within the 3,4-DHHCA molecule, and probably the coordination of adjacent phenolate sites can take place since the formation of AlL_2^{3-} complex ion by equilibrium (11) was supported by the potentiometric results. Then its formation constant was calculated by considering the occurrence of equilibrium (12). When $\log\beta$ values that were reported by several researchers[7,14,32)] in the Al(III)3,4-DHBA system are compared for the AlL_2^{3-}-type complex ion, our value is close to that of Kennedy and Powell.[7)] but other $\log\beta$ values are higher since they were determined at higher temperature and in a different ionic medium. They also did not take into account the formation of $Al(HL)_2^-$-type ion.

The hydrolysis of AlL_2^{3-} chelate was also considered in the $m=6.00$—7.00 range; due to the hydroxo complex formation in this pH range (6.11—6.98), readings were taken every 30 min. The related equilibrium constant for the assumed hydrolysis equilibrium (13) was also defined (Table 2). In the case of the 1 : 3 molar ratio of the Al(III) : 3,4-DHHCA system, the inflections were shifted to $m=6.00$. According to equilibrium (14) (in Table 2), the formation of $Al(HL)_3^{3-}$ chelate ion was assumed and its formation constant in the pH range 3.45—6.72 was calculated by introducing 224 experimental data. The results supported the formation of $Al(HL)_3^{3-}$ between $m=0.00$ and $m=6.00$. According to equilibrium (14) the carboxyl and phenolic proton that is in the *meta* position to the carboxyl proton were titrated and then salicylate-type coordination (COO^-, O^-) occurred in the $Al(HL)_3^{3-}$-type chelate ($m=0.00$—6.00 in acidic media). Due to the arrangement of donor groups within these ligands, catecholate sites act more efficiently and catecholate (O^-, O^-) type coordination occurs in $m=6.00$—9.00 range. As a result of change in binding mode, the formation of AlL_3^{6-} type coordination was proposed, and then the constant of equilibrium (16) was calculated for the Al(III) : ligand system (Table 2). Several authors[7,14,34)] reported AlL_3^{6-}-type coordination ions in the 1 : 3 Al(III) : 3,4-DHBA system. Our results also confirmed that the formation constants of Al(III) complexes of these three ligands decrease in the order 3,4-DHPA>3,4-DHBA>3,4-DHHCA, which is the order of $\Sigma\text{Log}\,K$ values of these ligands. Over the low pH range the salicylic acid-type mode of coordination predominates, while the catechol type is preferred in basic media.[26)]

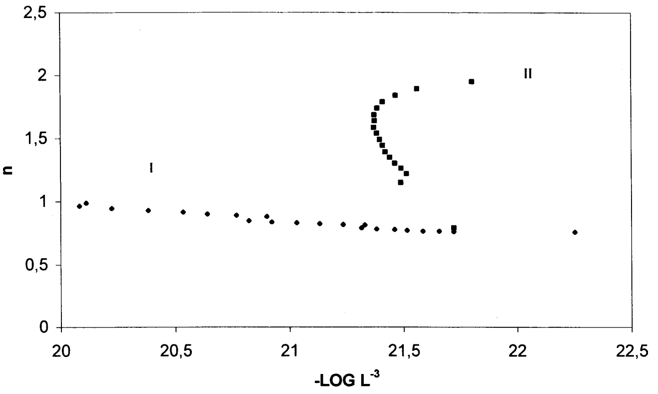

Fig. 5. Degree of Formation for Al(III) : 2,3-DHBA System, $\bar{n}$, as a Function of log L

I. (1 : 1) Al(III) : 2,3-DHBA. II. (1 : 2) Al(III) : 2,3-DHBA.

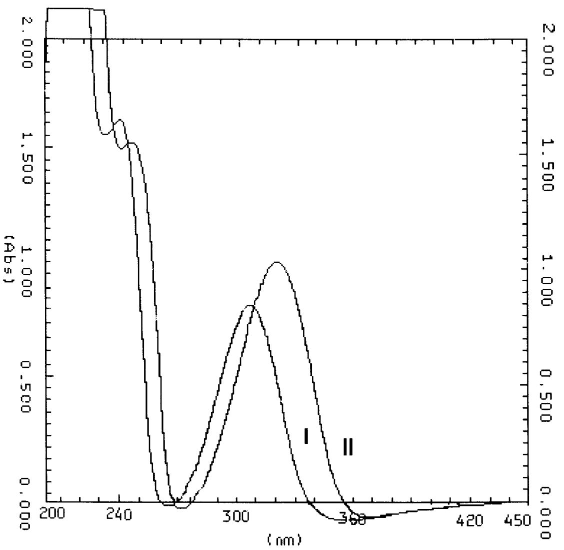

Fig. 6. Absorption Spectra of Al(III) Complexes of 2,3-DHBA in 0.1 M KCl at 25 °C (pH 3.05)

I. 2,3-DHBA alone ($T_L=6.0\times10^{-3}$ M). II. (1 : 1) Al(III) : 2,3-DHBA ($T_{Al}=6.0\times10^{-3}$ M, $T_L=6.0\times10^{-3}$ M).

Formation Curves The formation curves for Al(III) : 3,4-DHPA, Al(III) : 3,4-DHBA, and Al(III) : 3,4-DHHCA systems in different molar ratios were drawn (Fig. 7). They have one plateau at $\bar{n}=1.0$ for the 1 : 1 at $\bar{n}=2.0$ for the 1 : 2 and at $\bar{n}=3.0$ in for the 1 : 3 molar ratios of Al(III) to ligand. They indicate that the binding of one, two, and three moles of ligands were occured.

Speciation Diagrams To verify the existences of formed AlL, AlL_2^{3-} , and AlL_3^{6-} species in the Al(III) : 3,4-DHPA, Al(III) : 3,4-DHBA and Al(III) : 3,4-DHHCA systems, the concentration distribution curves of the complexes *versus* pH were drawn. The major species in defined pH ranges are AlL, AlL_2^{3-}, and AlL_3^{6-} complexes. The species distribution of the aluminium(III) complexes formed with 3,4-DHHCA at lig-

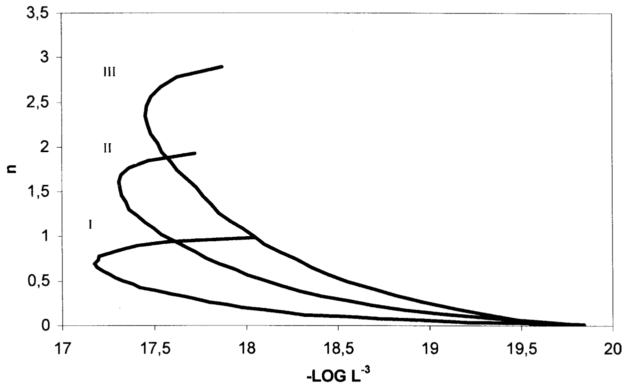

Fig. 7. Degree of Formation for Al(III) : 3,4-DHHCA System, $\bar{n}$, as a Function of log *L*

I. (1 : 1) Al(III) : 3,4-DHHCA. II. (1 : 2) Al(III) : 3,4-DHHCA. III. (1 : 3) Al(III) : 3,4-DHHCA.

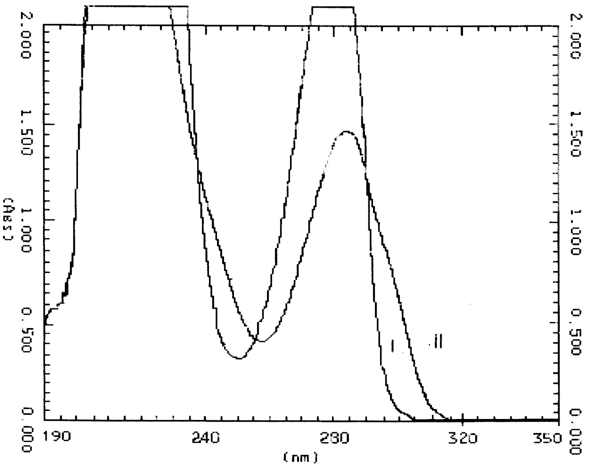

Fig. 8. Absorption Spectra of Al(III) Complexes of 3,4-DHHCA in 0.1 M KCl at 25 °C (pH 4.6)

I. 3,4-DHHCA alone (T_L=4.0×10^{-3} M). II. (1 : 1) Al(III) : 3,4-DHHCA (T_{Al}=4.0×10^{-3} M, T_L=4.0×10^{-3} M).

and to molar ratios of 1 : 1 and 1 : 2 as a function of pH are presented in Fig. 4.

Thus it was confirmed that the hydrolysis of either aqua Al(III) ion and Al(III) complexes can be hindered by catechol derivatives in 1 : 3 molar ratios of Al(III) : H_3L. 3,4-DHPA is the most convenient ligand.

Spectroscopic Results Either in 1 : 1 or 1 : 3 Al(III) : catechol derivative ligand systems the formation of AlL (type ion in the pH 4.29—4.86 range and AlL_3^{6-}-type coordination ion at pH 3.45—6.72 were determined from their potentiometric titration curves, respectively. For that reason, the interaction between Al(III) and 3,4-DHHCA was also investigated by spectrophotometry; the spectra of solutions in which Al(III) : 3,4-DHHCA ratios were 1 : 1 were taken at pH 4.85 (Fig. 8). The maximum absorbances were noticed at λ=300 nm for the 1 : 1 and 1 : 3 molar ratios. The pH of the solutions that have Al(III) molar fractions (X_M) in the 0.00—1.00 range were adjusted to 4.85 and 6.52; their absorbances were measured at λ=300 nm. They indicated maximum absorbances in solution at pH 4.60 and at X_M =0.5 that corresponding to the AlL^- type complex and in solution at pH 6.01 and at X_M=0.25 that means AlL_3^{6-}-type species exist.

Spectrophotometric evidence for the formation of AlL_2^{3-}-type complexes were confirmed in the pH 4.88—7.96 range for 3,4-DHPA, pH 4.07—5.96 range for 3,4-DHBA, and pH 5.52—8.41 range for 3,4-DHHCA by potentiometry. But due to the occurrence of $AlL_2(OH)^{4-}$-type complexes and their precipitation, the validities of AlL_2^{3-} complexes were not confirmed spectrophotometrically.

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