STABILITY CONSTANTS OF COMPLEXES OF TERVALENT CATIONS WITH HYDROXYPHENYLACETIC ACIDS

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Abstracts: *Potentiometric titrations were carried out for the determination of stability eonstants of the complexes of tervalent cations with hydroxyphenylacetie aeids. Evidence was provided by this method that only* Fe^{3+}, Al^{3+}, Ga^{3+} *and* In^{3+} *were capable of forming stable complexes. No evidence of complexation was found with* La^{3+} *and* Y^{3+}. *The correlation of the stability constants with the dissociation constants of the phenolic hydroxyl, with the radius of metal ions and with the ionization Potential of the metal ions are reported.*

Zusammenfassung: *Potentiomctrische Titrationen zur Bestimmung der Stabilitätskonstanten von Komplexen zwischen dreiwertigen Kationen und Hydroxyphenylessigsäuren wurden durchgeführt. Es konnte durch diese Methode nachgewiesen werden, daß nur* Fe^{3+}, Al^{3+}, Ga^{3+} *und* In^{3+} *in der Lage waren, stabile Komplexe zu bilden. Es konntc keine Komplex - Bildung mit* La^{3+} *und* Y^{3+} *festgestellt werden. Der Zusammenhang der Stabilitätskonstanten mit den Dissoziationskonstanten der phenolischen Hydroxylgruppe, mit dem Ionenradius der Metallen und mit dem Ionisationspotential der Metallionen wird angegeben.*

Although a great deal of work has been done on complex compounds, only a few papers deal with the influence of the functional group in the stability of metal complexes [1–5]. The present paper is a report of a more or less quantitative character concerning the influence of certain factors upon the stability of complexes of tervalents ions, Fe^{3+}, Al^{3+}, Ga^{3+} and In^{3+} with hydroxyphenylacetic acids.

Potentiometric titration appeared to be a suitable method for obtaining the desired information. Examination of the curves produced will indicate whether a complex formation takes place or not and the stability constants can be calculated from the pH measurements.

Mathematical treatment of the results was based on Bjerrum's[6] method. Considerable amount of work has been done utilizing the «formation function», $\bar{n}_M$, which may be expressed as follows:

$$\bar{n}_M = \frac{\sum\limits_{1}^{N} n\beta_n[L]^n}{\sum\limits_{o}^{N} \beta_n[L]^n} = \frac{C_L - \dfrac{(C_H - [H^+] + K_w[H]^{-1})}{\bar{n}_H}}{C_M} \qquad (1)$$

where $\bar{n}_M$ is the ratio of the bound ligand to the total metal ion present and $\bar{n}_M$ the average number of protons associated with the free ligand, not bound to the metal. Suppose, for simplicity that the formation of a mononuclear complex between a metal ion and a diprotic acid, i.e. Hydroxyphenylacetic acid, H_2PhA, takes place. Then the equilibrium ligand concentration will be:

$$[L] = \frac{\alpha}{\bar{n}_H} (C_H - [H^+]) \qquad (2)$$

where α the ratio of concentration of the ligand to the total concentration of the acid not bound to the metal ion.

Therefore, if the total concentration of the ligand and the central ion are known and the pH of the solutions are determined experimentally, it is possible to calculate α and $\bar{n}_H$, using the formulae (1) and (2) and then the formation function, $\bar{n}_M$ and the equilibrium ligand concentration respectively.

The acid dissociation of the H_2PhA is measured under the same conditions of temperature and ionic strength.

Under these conditions if the values of average formation constants, $\bar{n}_M$, are plotted versus the reciprocal values of equilibrium ligand concentration, [L], the stability constant may be determined graphically from the «formation curve» (Bjerrum's terminology) in which for $\bar{n}_M = 0{,}5$ the value of $\log 1/[L]$ represents the stability constant of the complex ML and for $\bar{n}_M = 1{,}5$ that of ML_2.

Experimental

Solutions of the complexing agents (0,1 M) of o-, m- and p-hydroxyphenylacetic acids were prepared by dissolving the calculated quantity of the compound in the solvent. Hydroxyphenylacetic acids (FERAK Berlin Co) were purified by recrystallization. Compounds of o-, m- and p - $HOC_6H_4CH_2COOCH_3$, o-, m- and p - $CH_3OC_6H_4CH_2COOH$ and 2 - hydroxynaphthylacetic acid were prepared according to the literature [7,8,9].

The m.p's of the compounds were in good agreement with those of the literature.

Commercial absolute ethanol was refluxed with a small amount of sodium and then distilled.

The Inorganic chemicals were of analytical grade and were used without further purification.

Iron (III)-, Indium (III)- and Ytrium (III) chloride solutions were prepared by dissolving $FeCl_3 . 6H_2O$, $InCl_3$ and $YCl_3 . 6H_2O$ in water in the presence of hydrochloric acid.

In a similar way the solutions of $AlCl_3$ and $GaCl_3$ were prepared by dissolving the calculated amount of aluminium wire and galium oxide in hydrochloric acid and then diluting with water. Solution of Lanthanium (III) nitrate was prepared in a similar way.

The solutions were standardized gravimetrically according to known methods [10,11] respectively.

Solutions of sodium hydroxide and potassium hydroxide were prepared from Titrisol Merck.

Potassium nitrate was used for standard ionic strength ($I = 0.1$).

A Beckman - Research pH - meter equipped with glass and calomel electrodes was used to measure hydrogen ion concentration. Calibration of the pH-meter was made before each set of reading the pH, against the standard buffer of pH = 4.00, 6.88 and 9.00 at 20° C. After completion of the whole set the calibration was again checked. All glass - ware used was Pyrex. The microburette was graduated to 0,01 ml.

The absorption spectra of the complexes were measured on a Zeiss PMQ II spectrophotometer.

The experiment method consisted of the titration with 0,10N sodium hydroxide of solutions containing the o-, m- and p - H_2PhA alone and in the presence of iron (III) chloride. Measurements were carried out at $20.00 \pm 0,02^0$ C in a jacketed titration glass cell of total capacity 100 ml, fitted with a magnetic stirrer, nitrogen inlet and outlet tubes, microburette and electrodes. Water from a thermostat circulated through the outer jacket.

All the titrating solutions whose ionic strength was maintained at approximately 0,1 were kept under a nitrogen atmosphere through titrations.

Results and Discussion

The experimental data were treated by means of eqns (1) and (2). The results of these calculations for Fe (III) are listed in Tables I, II and III.

TABLE I

Calculated $\bar{n}_{Fe}$ and p [o - PhA] values for the complex Fe(III) - o - H_2PhA $C_{Fe^{3+}} = 1{,}74 \, . \, 10^{-3}$ mol/lit, $C_{o\text{-}H_2PhA} = 1.10^{-2}$ mol/lit t = 20° C I = 0,1.

ml 0,1 N NaOH	pH	C_{H_2PhA} $\times 10^3$	$C_{Fe^{3+}}$ $\times 10^3$	$\bar{n}_H$	$\bar{n}_{Fe}$	$\alpha_{PhA^=}$ $\times 10^{10}$	$-\log[PhA^=]$
0,00	2,647	10,000	1,740	1,975	0,298	1,751	11,78
0,10	2,663	9,980	1,736	1,974	0,331	1,883	11,75
0,20	2,687	9,960	1,733	1,973	0,353	2,100	11,71
0,31	2,708	9,940	1,729	1,971	0,385	2,320	11,67
0,40	2,729	9,921	1,726	1,970	0,409	2,541	11,63
0,40	2,729	9,921	1,726	1,970	0,409	2,541	11,63
0,50	2,752	9,901	1,723	1,968	0,435	2,820	11,59
0,60	2,774	9,881	1,719	1,967	0,465	3,116	11,55
0,70	2,801	9,862	1,716	1,966	0,527	3,216	11,54
0,85	2,837	9,833	1,711	1,962	0,533	4,143	11,43
0,90	2,849	9,823	1,709	1,961	0,578	4,374	11,41
1,01	2,882	9,802	1,705	1,958	0,574	5,075	11,35
1,10	2,906	9,785	1,702	1,955	0,601	5,656	11,30
1,20	2,939	9,766	1,699	1,952	0,624	6,561	11,24
1,30	2,974	9,746	1,696	1,948	0,647	7,677	11,18
1,40	3,006	9,728	1,693	1,945	0,674	8,861	11,12
1,50	3,044	9,709	1,689	1,940	0,696	10,505	11,05
1,60	3,079	9,690	1,686	1,935	0,722	12,279	10,98
1,70	3,122	9,671	1,683	1,929	0,740	14,868	10,90
1,80	3,164	9,652	1,679	1,922	0,763	17,909	10,82
1,90	3,208	9,634	1,676	1,915	0,783	21,756	10,74
2,00	3,261	9,616	1,673	1,905	0,796	27,459	10,64
2,10	3,311	9,597	1,670	1,894	0,811	34,174	10,55
2,20	3,368	9,579	1,667	1,881	0,819	43,805	10,44
2,30	3,425	9,560	1,663	1,867	0,825	56,013	10,34
2,40	3,483	9,542	1,660	1,850	0,829	71,790	10,23
2,50	3,541	9,524	1,655	1,833	0,832	91,888	10,12
2,60	3,601	9,506	1,654	1,812	0,827	118,040	10,02
2,70	3,657	9,488	1,651	1,792	0,826	149,093	9,92

TABLE II

Calculated $\bar{n}_{Fe}$ and p [m - PhA] values for the complex Fe(III) - m - H_2PhA
$C_{Fe^{3+}} = 1{,}74.10^{-3}$ mol/lit, $C_{m\text{-}H_2PhA} = 1.10^{-2}$ mol/lit t = 20° C I = 0,1

ml 0,1 N NaOH	pH	C_{H_2PhA} $\times 10^3$	$C_{Fe^{3+}}$ $\times 10^3$	$\bar{n}_H$	$\bar{n}_{Fe}$	$\alpha_{PhA^=}$ $\times 10^0$	—log[PhA=]
0,00	2,752	10,000	1,740	1,961	0,116	2,073	10,69
0,10	2,773	9,980	1,736	1,959	0,146	2,279	10,65
0,20	2,795	9,960	1,733	1,957	0,175	2,516	10,61
0,30	2,817	9,940	1,730	1,955	0,205	2,779	10,57
0,40	2,838	9,921	1,726	1,952	0,238	3,054	10,54
0,50	2,864	9,901	1,723	1,950	0,264	3,432	10,49
0,60	2,885	9,881	1,719	1,947	0,29	3,771	10,45
0,70	2,911	9,862	1,716	1,944	0,327	4,237	10,40
0,80	2,935	9,842	1,712	1,941	0,359	4,718	10,36
0,90	2,957	9,823	1,709	1,938	0,384	5,205	10,32
1,00	2,982	9,804	1,706	1,935	0,426	5,817	10,28
1,10	3,009	9,785	1,702	1,931	0,456	5,662	10,23
1,20	3,037	9,766	1,699	1,927	0,486	7,430	10,18
1,30	3,063	9,746	1,696	1,921	0,508	8,716	10,11
1,40	3,089	9,728	1,693	1,918	0,551	9,355	10,08
1,50	3,113	9,709	1,689	1,914	0,587	10,401	10,04
1,60	3,142	9,690	1,686	1,909	0,618	11,817	9,99
1,70	3,172	9,671	1,683	1,903	0,646	13,478	9,94
1,80	3,201	9,652	1,679	1,897	0,678	15,303	9,89
1,90	3,233	9,634	1,676	1,890	0,706	17,592	9,83
2,00	3,263	9,615	$1^{1}73$	1,883	0,737	20,044	9,77
2,10	3,295	9,597	1,670	1,874	0,766	23,020	9,72
2,20	3,329	9,578	1,667	1,866	0,791	26,033	9,67
2,30	3,367	9,560	1,663	1,856	0,813	31,387	9,59
2,40	3,403	9,542	1,660	1,845	0,837	36,565	9,53
2,50	3,441	9,524	1,657	1,833	0,857	42,980	9,46
2,60	3,480	9,506	1,654	1,820	0,875	4,605	9,39
2,70	3,520	9,488	1,651	1,806	0,891	59,777	9,32
2,80	3,562	9,470	1,648	1,790	0,903	71,166	9,25
2,90	3,603	9,452	1,645	1,775	0,916	84,616	9,17
3,00	3,645	9,435	1,641	1,758	0,928	99,864	9,10
3,10	3,686	9,416	1,638	1,740	0,937	117,784	9,03
3,20	3,725	9,398	1,635	1,722	0,948	137,695	8,97
3,30	3,769	9,381	1,632	1,701	0,951	163,000	8,89
3,40	3,810	9,363	1,629	1,681	0,957	192,069	8,82
3,50	3,847	9,346	1,626	1,662	0,967	221,666	8,76
3,60	3,888	9,328	1,623	1,641	0,970	259,035	8,70
3,70	3,927	9,311	1,620	1,620	0,975	299,151	8,64
3,80	3,967	9,294	1,617	1,598	0,978	346,709	8,57

TABLE III

Calculated $\bar{n}_{Fe}$ *and p [p - PhA] values for the complex Fe (III) - p -* H_2PhA
$C_{Fe^{3+}}$ $1{,}74.10^{-3}$ = *mol/lit,* $C_{p\text{-}H_2PhA} = 1.10^{-2}$ *mol/lit* $t = 20^{\circ}$ *C,* $I = 0{,}1$

ml 0,1 N NaOH	pH	C_{H_2PhA} $\times 10^3$	$C_{Fe^{3+}}$ $\times 10^3$	$\bar{n}_H$	$\bar{n}_{Fe}$	$\alpha_{PhA^=}$ $\times 10^9$	—log[PhA=]
0,00	2,769	10,000	1,740	1,969	0,120	1,443	10,85
0,10	2,789	9,980	1,736	1,968	0,153	1,580	10,81
0,20	2,811	9,960	1,733	1,966	0,184	1,746	10,77
0,30	2,830	9,940	1,730	1,964	0,220	1,903	10,74
0,40	2,855	9,921	1,726	1,962	0,249	2,130	10,69
0,50	2,876	9,901	1,723	1,961	0,284	2,343	10,66
0,60	2,900	9,881	1,719	1,959	0,317	2,610	10,61
0,70	2,923	9,862	1,716	1,956	0,346	2,948	10,56
0,80	2,943	9,842	1,712	1,954	0,389	3,168	10,54
0,91	2,969	9,821	1,709	1,952	0,427	3,561	10,49
1,00	2,992	9,804	1,706	1,949	0,458	3,949	10,45
1,10	3,018	9,785	1,702	1,946	0,492	4,437	10,40
1,20	3,041	9,766	1,699	1,944	0,529	4,919	10,36
1,30	3,068	9,746	1,696	1,940	0,563	5,550	10,31
1,40	3,093	9,728	1,693	1,937	0,599	6,206	10,27
1,50	3,118	9,709	1,689	1,930	0,628	7,616	10,18
1,60	3,149	9,690	1,686	1,929	0,668	7,962	10,17
1,70	3,176	9,671	1,683	1,925	0,702	8,975	10,12
1,80	3,205	9,652	1,679	1,920	0,738	10,204	10,07
1,90	3,236	9,634	1,676	1,914	0,771	11,701	10,01
2,01	3,262	9,613	1,673	1,909	0,814	13,120	9,97
2,12	3,311	9,593	1,669	1,900	0,838	16,265	9,88
2,20	3,340	9,578	1,667	1,894	0,860	18,465	9,82
2,30	3,379	9,560	1,663	1,885	0,886	21,882	9,75
2,39	3,417	9,544	1,661	1,894	0,860	18,465	9,82
2,30	3,379	9,560	1,663	1,885	0,886	21,882	9,75
2,39	3,417	9,544	1,661	1,876	0,906	25,793	9,68
2,55	3,481	9,515	1,655	1,859	0,945	33,978	9,57
2,60	3,504	9,506	1,654	1,852	0,953	37,491	9,53
2,70	3,547	9,488	1,651	1,839	0,973	44,997	9,45
2,80	3,569	9,470	1,648	1,823	0,983	55,323	9,36
2,90	3,641	9,452	1,645	1,808	0,999	66,799	9,28
3,00	3,694	9,435	1,641	1,788	1,002	83,144	9,19
3,10	3,743	9,416	1,638	1,769	1,007	101,773	9,10

Figure I shows the formation curves of the above complexes. Similar curves are also obtained for the other metal ions. The «formation curve» clearly suggest the formation of the 1 : 1 complex only. The value of $\bar{n}_M$ was always less 1. The results are summarized in Table IV. No evidence of complexation was found with La^{3+} and Y^{3+}.

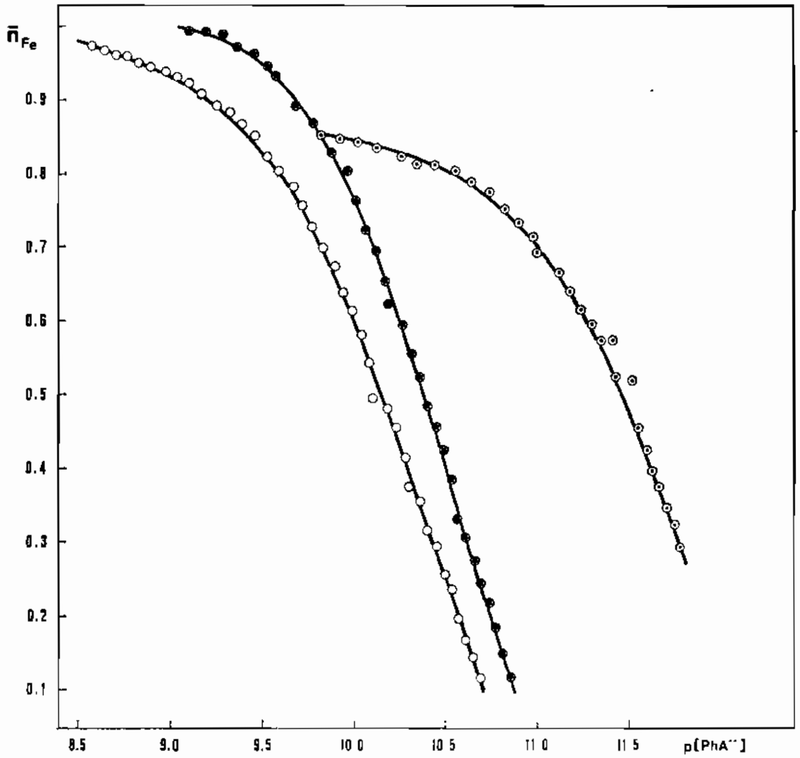


Fig. 1.

Formation curves of complexes between Iron (III) ions and o-, m- and p - hydroxyphenylacetic acids.

⊙ = *o* - H_2PhA, = *m* - H_2PhA, ✱ = *p* - H_2PhA.

T A B L E IV

Stability Constants of metal complexes of hydroxyphenylacetic acids

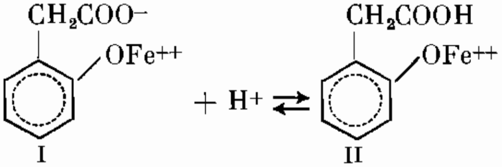
Metal ion	log β		
	o - H_2PhA	m - H_2PhA	p - H_2PhA
Fe^{3+}	11,35	10,20	10,40
Al^{3+}	11,65	10,75	10,90
Ga^{3+}	11,50	10,60	10,75
In^{3+}	11,20	10,30	10,45

The value of logβ of the complex Fe (III)- o - H_2PhA obtained by the spectrophotometric method closely agress with that obtained using the potentiometric method[12].

To obtain a more reliable value of logβ a large of excess of the ligand was used. For a series where the ratio of total ligand to total metal ion concentrations varied from 1 : 1 to 1 : 20 the values of logβ show approximately only minor differences.

It should be mentioned that for study of solutions complexes of metal chlorides instead of perchlorates were used because the addition of sodium perchlorate destroyes the characteristic violet color of the compounds of Iron (III) ions with hydroxyphenylacetic acids. This leads us to the suggestion that the perchlorate ions hinder the formation of these complexes.

Considering the proposed structures for the complexes of Iron (III) with hydroxybenzoic acids and their derivatives we may by analogy suggest the structure for the complexes of Iron (III) with o-, m- and p - hydroxyphenylacetic acids[13,14,15]. For example the structure of Fe - o - H_2PhA is probably:



I

II

The dissociated form (I) in solution is predominant in the studied pH range over that of (II). More evidence on this point has been obtained by the results of the spectrophotometric method which gave the value of log β ca. 12. It is thus clear that the calculated constant refers to the structure (I) because the potentiometric titration for the structure (II) gives log β ca. 9.

Hydroxynaphthylacetic acid was also studied as ligand. It has been found that the later causes a bathochromic shift of the maximum intensity to longer wave - lengths (from $\lambda_{max} = 545$ nm to $\lambda_{max} = 620$ nm).

These observations support the suggestion that the naphthalene ring offers more resonating structures compared with that of the benzene ring. In concequence there is a reduction of energy between the initial energy state and the excited state of the complex.

The stability constant of the complex iron (III) - 2 - hydroxynaphthylacetic acid was also investigated potentiometrically in water - ethanol solution (35 per cent by volume). The value of log β was found = 13.30 ± 0.05. A similar titration of Fe (III) - o - H_2PhA in ethanol - water solution (35 : 100 v/v) showed that the value of log β was 13.70 ± 0,05 and the pK = 11.65 ± 0,03.

These observations suggest that the introduction of the second benzene ring does not modify the stability of these complexes of iron (III).

For all these complexes it was found that the stability constants depend upon the pK of the phenolic group of the acids (pK_2).

It has been found that a more stable complex was formed when the ionization constant of the phenolic group was weaker. A supporting evidence has been the determination of stability constants of methylester derivatives of hydroxyphenylacetic acids in ethanol - water mixture. The results obtained for log β and pK_2 are given in table V.

TABLE V

Acid dissociation constants and stability constants of complexes of methyl hydroxyphenylacetates with Fe(III) - ions in 35 % ethanol - water.

Methylester	pK	logβ
o - H PhA	10,95	9,85
m -	10,85	9,60
p -	10,80	9,50

It has been observed that the sterification of the carboxylic gronp, causes an increase in the pK. Furthermore, the stronger ionization of the phenolic group has as a result the lowering of the stability constants of the respective complexes.

This is in accordance with the expected inductive effect. The weaker acid character of the phenolic group in the case of o - H_2PhA over that of the respective ester may contrivute to the fact that the dissociation of the carboxylic group has been completed before the dissociation of the phenolic hydroxyl. As a result the phenolic hydroxyl becomes less acidic because of the influence of the +I inductive effect by the already ionized carboxylic group.

It appears that the stability constants depend upon the basicity of the ligand in agreement with the conclusions reached by Bjerrum[16] and Schwarzenbach[17] a general linear relation exists between the log β of a series of 1 : 1 complexes and the pK of ligands with a similar structure. The general form

$$\log \beta = \sigma \, pK + \tau \tag{3}$$

where σ and τ are constants, was first used by the above athors and much discussed by Martell and Calvin[18].

Calvin and Wilson[3] found a rough linear relation between log β and pK for many salicylaldehyde derivatives. A somewhat larger deviation was observed for naphthaldehyde complexes. In this case the dissociation constant of the phenolic group is used as a measure of the basicity of complexes. These authors suggest that for all the series of complexes σ is approximately the same but τ changes. Jones[19] et al based in these results have suggested that the equation (3) is an over-simplification and that the relation between log β and pK is more comlex.

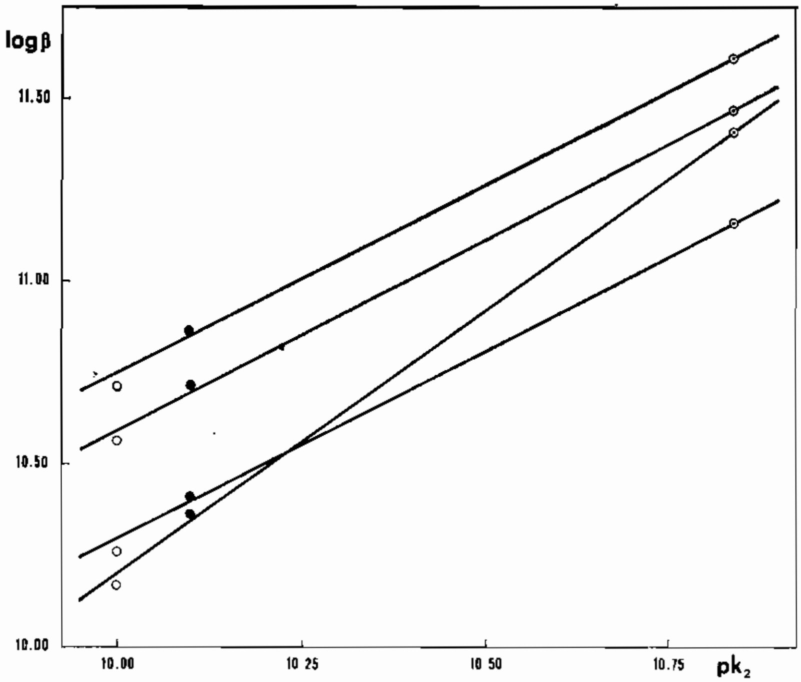


Fig. 2.

Relationship between the dissociation constaant of the phenolic group of hydroxphenylacetic acids and the stability constant of their complexes with tervalent ions.

It has been shown that there is a correlation between log β and

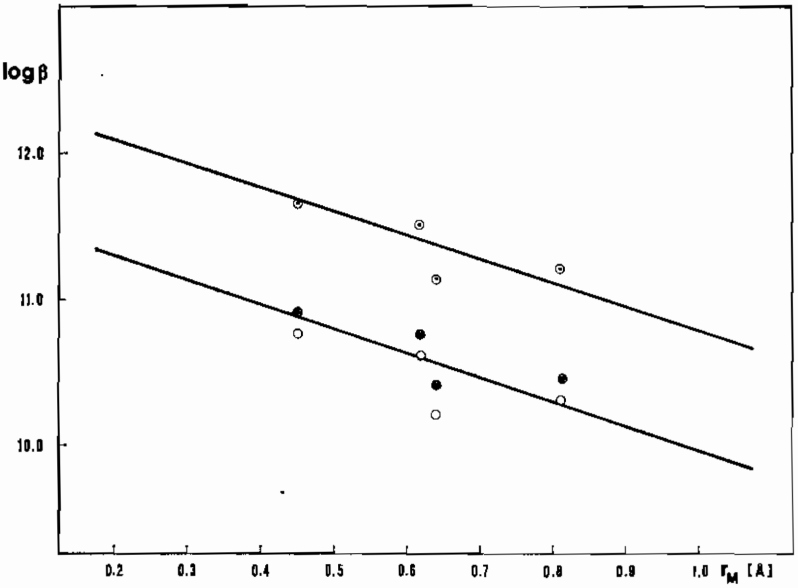


Fig. 3.
Relationship between log β of complexes of hydroxyphenylacetic acids and ionic radius of the tervalent ions.

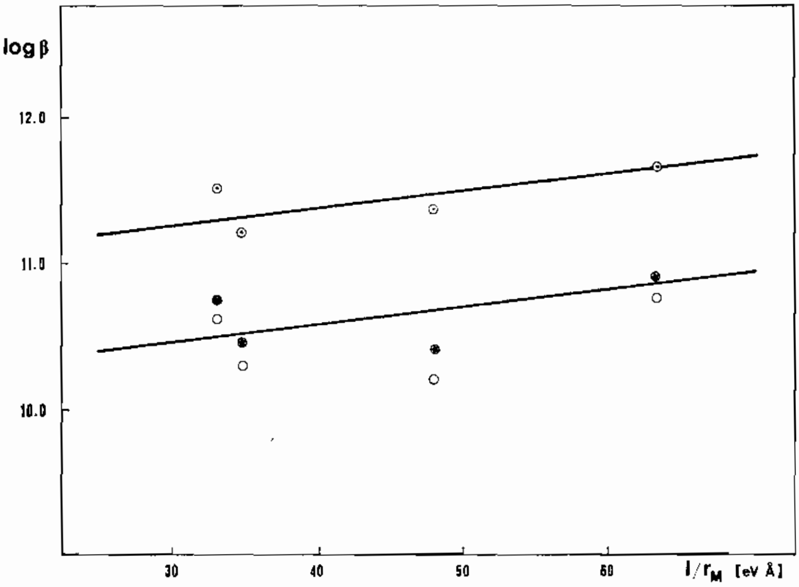


Fig. 4.
Depcdence of log β versus the ionization potential - radius ratio of the tervalent ions

pK and this is a measure of the bond strength. This is in agreement with the above authors. In fact the greater the tendency of the metal to bound with the ligand the more stable the complexes formed. This is illustrated in fig. 2 where log β is plotted as a function of pK_2.

Irving and Williams [20] further showed for the bivalent ions of transition metals that the stability constants have a linear relationship with ionization potential of metal ions. By analogy Martell and Plumb [21] found that log β depends on the ionic radius of the metals.

Fig. 3 gives data for the complexes of Fe^{3+}, Al^{3+}, Ga^{3+} and In^{3+} with o-, m- and p - H_2PhA.

A similar variation in stability should be expected for the dependence of log β versus the ionization potential - radius ratio. In fact the plots of log β versus I/r_M are shown in fig. 4.

The log β data in fig. 2 are distributed into two distinct lines. They are (i) the line of unit slope for Al^{3+}, Ga^{3+} and In^{3+} and (II) the line of slope 1,31 for Fe^{3+}. It seems that steric factors are operative for the later complex and they lower the stability constant.

ΣΤΑΘΕΡΑΙ ΣΤΑΘΕΡΟΤΗΤΟΣ ΣΥΜΠΛΟΚΩΝ ΤΩΝ ΤΡΙΣΘΕΝΩΝ ΚΑΤΙΟΝΤΩΝ ΜΕΤΑ ΤΩΝ ΥΔΡΟΞΥ- ΦΑΙΝΥΛΟΞΙΚΩΝ ΟΞΕΩΝ

ὑπὸ

Δ. ΓΙΑΝΝΑΚΟΥΔΑΚΗ καὶ Π. ΚΑΡΑΓΙΑΝΝΙΔΗ

Ἐκ τῶν Ἐργαστηρίων Φυσικῆς Χημείας καὶ Ἀνοργάνου Χημείας
τοῦ Πανεπιστημίου Θεσσαλονίκης

Μελετᾶται διὰ τῆς ποτενσιομετρικῆς μεθόδου ὁ σχηματισμὸς συμπλόκων ἑνώσεων μεταξὺ τῶν ὑδροξυφαινυλοξικῶν ὀξέων καὶ τῶν τρισθενῶν κατιόντων καὶ προσδιορίζονται αἱ τιμαὶ τῆς σταθερᾶς σταθερότητος αὐτῶν εἰς τὴν θερμοκρασίαν τῶν 20⁰ C καὶ δι᾽ ἰονικὴν ἰσχὺν 0,1. Διαπιστοῦται ὅτι μόνον τὰ κατιόντα Fe^{3+}, Al^{3+}, Ga^{3+} καὶ In^{3+} εἶναι εἰς θέσιν νὰ σχηματίσουν σχετικῶς σταθερὰ σύμπλοκα. Εὑρίσκεται ὅτι μεταξὺ τῶν προσδιορισθεισῶν τιμῶν τῆς σταθερᾶς σταθερότητος καὶ τῶν ἀντιστοίχων τιμῶν τοῦ pK τοῦ φαινολικοῦ ὑδροξυλίου τῶν χρησιμοποιηθέντων ὑδροξυφαινυλοξικῶν ὀξέων ὑφίσταται γραμμικὴ συνάρτησις. Ὅσον ἀσθενέστερος εἶναι ὁ ὄξινος χαρακτὴρ τῆς φαινολικῆς ὁμάδος, τόσον σταθερώτερον εἶναι τὸ σχηματιζόμενον σύμπλοκον. Παρέχεται τέλος ἡ σχέσις μεταξὺ τῶν εὑρεθεισῶν τιμῶν τῆς σταθερᾶς σταθερότητος τῶν μελετηθέντων συμπλόκων καὶ τῆς ἀκτῖνος τῶν χρησιμοποιηθέντων κατιόντων, ὡς καὶ τοῦ δυναμικοῦ ἰονισμοῦ τῶν ἀντιστοίχων μετάλλων.

BIBLIOGRAPHY

1. P. Pfeiffer : Angew, Chem. 53 93 (1940)
2. H. Diehl : Chem. Rev. 21 39 (1937)
3. M. Calvin *and* K. W. Wilson : J. Am. Chem. Soc. 67 2003 (1945)
4. H. Irving *and* H. S. Rossoti : J. Chem. Soc. 2910 (1954)
5. A. E. Martell *and* M. Calvin «Chemistry of the Metal Chelate Compounds» p. 134, 5th ed. Prentice - Hall, inc. N. J. 1962
6. J. Bjerrum: «Metal Amine Formation in Aqueous Solutions», P. Haase and Son, Copenhagen (1941)
7. J. Levine, T. E. Eble *and* H. Fisghbach: J. Am. Chem. Soc. 70 1930 (1948), A. Vogel «Practical Organic Chemistry» 379, 3rd Ed. Longmans 1964
8. J. F. Collixs *and* H. Smith : J. Chem. Soc. 4308 (1956)
   A. Vogel : «Practical Organic Chemistry» p. 365, 3rd Ed. Longmans 1964
9. M. M. Furman, J. H. Thelin, D. W. Hein *and* W. B. Hardy : J. Am. Chem. Soc. 82 1450 (1960)
10. A. I. Vogel : «Quantitative Inorganic Analysis» p.p. 468, 472, 516, Longmans, 3rd Ed. London 1961
11. F. J. Welcher : «Org. Anal. Leagents» vol. 1 p.p. 292, 311, vol III p. 387, Van Nostrand Co Inc. 2nd N. York, 1948
12. P. Karayannidis : Dissertation, Univ. of Thessaloniki (1968)
13. Colette Bertin - Batsch : Ann. de Chim. 7 481 (1952)
14. P. H. Core *and* P. J. Newman : Anal. Chem. Acta 31 111 (1964)
15. A. K. Babko: Zavodskaya Lab. 13 645 (1947), S. S. Katiyar *and* V. B. S. Chakhan J. In. Nucl. Chem. 25 1375 (1963)
16. J. Bjerrum : Chem. Rev. 46 381 (1950)
17. G. Schwarzenbach, G. Anderegg, W. Schnrider *and* H. Senn: Helv. Chim. Acta 38 1147 (1955)
18. A. E. Martrll *and* M. Calvin: «The chemistry of the Metal Chelates» p. 76 Prentice - Hall 5th Ed.,*e*N. Y., 1962
19. J. G. Jones, J. B. Poole, J. C. Tomkinson *and* R. J. P. Williams : J. Chem. Soc. 1958 2001
20. H. Irving *and* R. J. P. Williams : Nature 162 746 (1948)
21. C. Plumb, A. E. Martell *and* E. C. Bersworth: J. Phys. and Colloid Chem. 54 1208 (1950)