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The Complex Formation between Iron(III)Ion and Some Phenols. III. Salicylaldehyde, *o*-Hydroxyacetophenone, Salicylamide and Methyl salicylate

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The complex formation between iron(III)ion and the following phenolic substances has been investigated: salicylaldehyde, *o*-hydroxyacetophenone, salicylamide and methyl salicylate. All measurements have been made at 25.0° ± 0.1° C and in solutions with a concentration of ClO_4^- of 3 000 mC. By potentiometric and photometric methods the complexity constants, defined as follows have been determined

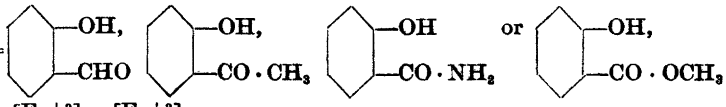
$$\varkappa_n = \frac{[H^+]^n[FeR_n^{3-n}]}{[RH]^n[Fe^{+3}]} \quad (n = 1 \text{ or } 2)$$

RH is the phenolic substance concerned. Further the molar extinctions (1 000 ε_n) have been determined. The results are listed in Table 12.

In the previous works in this series the complex formation between iron(III)-ion and some chelating phenols have been studied, namely sulfosalicylic acid [1], salicylic acid and *p*-aminosalicylic acid [2]. In this work the complex formation with salicylaldehyde, *o*-hydroxyacetophenone, salicylamide and methyl salicylate is investigated. All these substances may give chelate complexes with iron(III)ion.

Symbols used in the text (mC denotes millimoles/liter).

h = hydrogen ion concentration, mC.
[] = concentration of substance indicated, mC.
$[]_t$ = stoichiometrical concentration, mC.

RH = 

$$b = \frac{[Fe^{+3}]_t - [Fe^{+3}]}{[Fe^{+3}]}$$

ε = extinction, $cm^{-1}mC^{-1}$
E = extinction, cm^{-1}
$\varkappa_n$ = complexity constant
$\varkappa_{nm}$ = complexity constants of the hydroxyl complexes $Fe_n(OH)_m$

$$\varkappa' = \frac{\varkappa_{11}}{h} + \frac{\varkappa_{12}}{h^2} + \frac{2\varkappa_{22}[Fe^{+3}]}{h^2}$$

The signs for the electrical charges are omitted when there is no risk of confusion.

The complexes are formed according to the following equation

$$Fe + n\ RH = n\ H + FeR_n$$

and the complexity constants are defined as follows:

$$\varkappa_n = \frac{h^n[FeR_n]}{[RH]^n[Fe]} \quad (n = 1,\ 2\ldots) \tag{1}$$

The same equations are valid whether or not chelates are formed. In either case only one hydrogen ion is set free per RH molecule.

In determining the complexity constants the same methods have been used as in the previous works [1,2]. However, in this investigation some complications are met with. The substances studied are only slightly soluble (5—15 mC) in the medium used, 3 000 mC $NaClO_4$, at 25° C. Due to this only the lowest complexes are formed, FeR and perhaps FeR_2. More than two molecules R per atom Fe have not been found. Due to the low complex forming tendency and the low concentration of R the hydroxyl complexes of iron(III)ion have been formed in higher amounts, appreciably influencing the calculations.

In the potentiometric determinations the following equation, derived before, has been used:

$$\frac{(b-\varkappa')h}{[RH]} = \varkappa_1 + \varkappa_2 \frac{[RH]}{h} + \ldots \tag{2}$$

$\varkappa'$, which in the earlier investigations was a small correction term, is now of the same order as b. This causes uncertainties in the results.

In the photometric determinations the following equations, also derived before, have been used:

$$\frac{c}{E} = \frac{1}{\varepsilon_1} + \frac{h}{[RH]} \frac{1}{\varkappa_1\varepsilon_1} \tag{3}$$

which is valid when $[Fe]_t = [R]_t = c$, and when only FeR is formed in measurable amount.

$$\frac{[Fe]_t}{E} = \frac{1}{\varepsilon_1} + \frac{h}{[RH]} \frac{1}{\varepsilon_1\varkappa_1} \tag{4}$$

$$\frac{[Fe]_t}{E} = \frac{1}{\varepsilon_2} + \frac{h}{[RH]} \frac{E-[Fe]_t\varepsilon_1}{E} \frac{\varkappa_1}{\varepsilon_2\varkappa_2} \tag{5}$$

Equations (4) and (5) are valid when $[R]_t \gg [Fe]_t$. Equ. (4) is used in a range where only FeR is formed in measurable amount. Equ. (5) is used when FeR and FeR_2 are formed, but no other forms of Fe are present.

Equations (3)—(5) were derived assuming that no appreciable amounts of hydroxyl complexes are formed.

Apparatus and chemicals. The same apparatus has been used as in previous investigations [1].

The preparation and quantitative determination of $Fe(ClO_4)_3$, $Fe(ClO_4)_3$ and $NaClO_4$ have been described earlier.

Salicylaldehyde was purified as the bisulfite compound and by freezing out. *o*-Hydroxyacetophenone was made according to Rosenmund and Schnurr [3] by heating phenyl

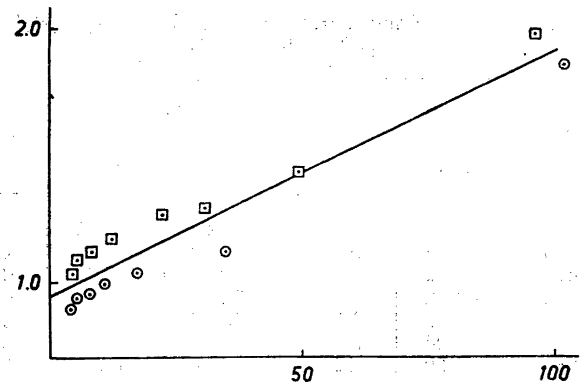


Fig. 1. Salicylaldehyde. Potentiometric determination of $\varkappa_1$ *and* $\varkappa_2$. $\frac{(b-\varkappa')h}{[RH]}$ *vs.* $\frac{[RH]_t}{h}$.
○ : Fe(III) = 0.1051 mC, □ : Fe(III) = 0.0496 mC.

acetate and water-free $AlCl_3$. The raw product was purified by steam distillation. This product was colourless. The salicylamide used had a melting point 138–139° C.

The quality of the methyl salicylate used was controlled according to the Swedish Pharmacopeia Ed. XI. It contained no free acid.

All the solutions were made up by weight, and $NaClO_4$ added to a total concentration of 3 000 mC ClO_4^-. Under these conditions it is assumed that the activity factors are constant and hence the concentrations may be used instead of activities in the equilibria.

SALICYLALDEHYDE

The complex formation between iron(III)ion and salicylaldehyde has been studied by Herbst and coworkers [4] and by Broumand and Smith [5]. They have shown, using the method of continuous variations [6] that the complex is built up from one molecule of salicylaldehyde per atom Fe. The complex formation between salicylaldehyde and bivalent metals has been thoroughly investigated

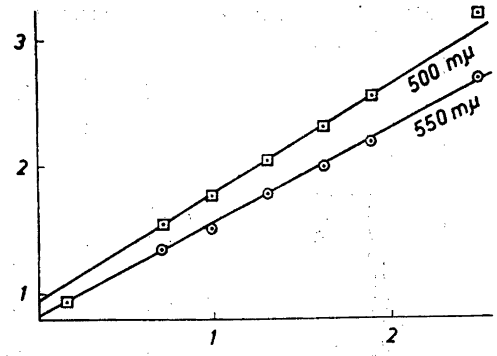


Fig. 2. Salicylaldehyde. Photometric determination of $\varkappa_1$. $[Fe]_t/E$ *vs.* $h/[RH]$.
$[R]_t$ = 6.664 mC, $[Fe]_t$ = 0.696 mC.

Table 1. Salicylaldehyde. Photometric determination of $\varkappa_1$. $[Fe]_t = 0.696$ mC; $[R]_t = 6.664$ mC

h	Extinction at wave length						
	400	450	500	550	600	650	700
1.012	0.828	0.562	0.740	0.845	0.661	0.422	0.242
4.708	0.500	0.327	0.452	0.513	0.419	0.265	0.155
6.604	0.461	0.300	0.392	0.458	0.363	0.237	0.133
8.740	0.398	0.252	0.337	0.390	0.316	0.203	0.112
10.82	0.345	0.219	0.300	0.347	0.270	0.174	0.100
12.65	0.321	0.204	0.272	0.317	0.256	0.160	0.090
16.67	0.263	0.160	0.218	0.259	0.208	0.131	0.072

and it is generally assumed that a chelate is formed. Some of these metals form complexes with 1 or 2 molecules of aldehyde per metal atom.

In the potentiometric investigation of this complex formation, this author has shown that complexes with 1 and 2 molecules per atom Fe are formed. However, the higher complex has such a low stability that it was impossible to make a photometric investigation because only a very small fraction of the complex-bound iron was contained in the form of the complex FeR_2 even when [RH]/h was made as high as possible.

Salicylaldehyde is slightly soluble (*ca.* 10 mC) in 3 000 mC $NaClO_4$ at 25° C. Thus, it was impossible to work with high concentrations of iron without the OH-complexes becoming dominant. Only two concentrations of Fe(III) have been studied in the potentiometric measurements. The results of these experiments are shown in Fig. 1. From these curves the values of $\varkappa_1$ and $\varkappa_2$ are calculated and given in Table 12.

The photometric determinations are shown in Table 1 and Fig. 2. This figure shows the curves at two wave lengths, the values being calculated with equ. (3). The results are given in Table 12.

Table 2. o-Hydroxyacetophenone. Potentiometric determination of $\varkappa_1$. $[Fe]_t = 0.1051$ mC. Result: $\varkappa_1 = 0.43$ (mean value).

h	b	$\frac{[RH]}{h}$	$\frac{(b-\varkappa')\,h}{[RH]}$
1.646	4.0881	7.787	0.429
1.258	5.4517	10.165	0.437
0.9656	7.5052	13.218	0.455
0.6776	10.886	18.803	0.449
0.4085	18.260	31.141	0.419
0.3286	23.998	38.691	0.430
0.2482	33.129	51.201	0.418
0.1882	48.591	67.487	0.442
0.1321	84.516	96.101	0.515
0.1079	149.95	117.60	0.845

Table 3. o-Hydroxyacetophenone. Potentiometric determination of $\varkappa_1$. $[Fe]_t = 0.0496$ mC. Result: $\varkappa_1 = 0.70$ (mean value).

h	b	$\frac{[RH]}{h}$	$\frac{(b-\varkappa')h}{[RH]}$
1.225	8.2296	10.545	0.679
0.8794	11.670	14.660	0.682
0.5843	17.962	22.026	0.680
0.3469	32.083	37.042	0.685
0.2158	57.170	59.500	0.680
0.1776	72.758	72.280	0.721
0.1122	136.49	114.349	0.783

Table 4. o-Hydroxyacetophenone. Photometric determination of $\varkappa_1$. $[R]_t = 11.91$ mC; $[Fe]_t = 0.696$ mC.

h	Extinction at wave length						
	400	450	500	550	600	650	700
1.069	0.705	0.480	0.708	0.803	0.615	0.390	0.225
3.021	0.555	0.364	0.541	0.620	0.500	0.318	0.180
5.089	0.470	0.294	0.450	0.504	0.412	0.254	0.147
7.166	0.400	0.248	0.378	0.436	0.346	0.211	0.120
9.086	0.359	0.215	0.335	0.380	0.300	0.184	0.110
11.13	0.318	0.200	0.300	0.340	0.270	0.172	0.096
13.00	0.288	0.176	0.266	0.303	0.235	0.146	0.084

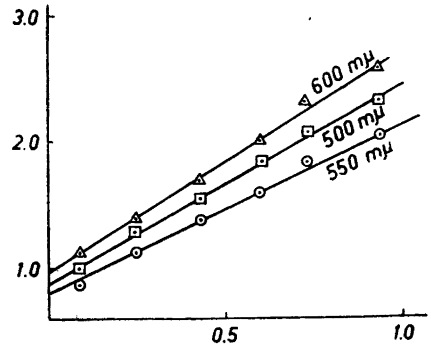


Fig. 3. o-Hydroxyacetophenone. Photometric determination of $\varkappa_1$. $[Fe]_t/E$ *vs.* h/[RH]. $[R]_t = 11.91$ mC, $[Fe]_t = 0.696$ mC.

o-HYDROXYACETOPHENONE

Recently, Jatkar and Mattoo [11] have published a work where they show the formation of complexes with one molecule of *o*-hydroxyacetophenone per atom Fe. They have determined the complexity constant $K_1 = [Fe][R]/[FeR] = 14 \cdot 10^{-4}$ C, where they assume [R] = [RH]. However, this value of the constant is of little interest as no pH measurements seem to have been made.

Table 5. Salicylamide. Potentiometric determination of $\varkappa_1$ and $\varkappa_2$. $[Fe]_t = 0.484$ mC. Results: $\varkappa_1 = 13.7$; $\varkappa_2 = 0.21$.

h	b	$\frac{[RH]}{h}$	$\frac{(b-\varkappa')h}{[RH]}$
0.9107	50.961	3.413	14.46
0.7211	64.887	4.298	14.58
0.5556	85.520	5.558	14.80
0.4150	117.59	7.405	15.20
0.3607	136.49	8.514	15.29
0.3209	157.17	9.520	15.71
0.2757	185.98	11.055	15.94
0.2415	218.33	12.555	16.41
0.2028	269.63	14.911	16.98

Table 6. Salicylamide. Potentiometric determination of $\varkappa_1$ and $\varkappa_2$. $[Fe]_t = 0.484$ mC. Results: $\varkappa_1 = 13.0$; $\varkappa_2 = 0.53$.

h	b	$\frac{[RH]}{h}$	$\frac{(b-\varkappa')h}{[RH]}$
1.595	26.767	1.807	14.38
1.200	36.326	2.398	14.69
0.7918	56.719	3.665	14.94
0.4849	96.996	5.865	15.85
0.2434	224.39	11.27	18.84
0.1342	509.40	20.06	23.69
0.1079	729.17	24.42	27.79

Table 7. Salicylamide. Potentiometric determination of $\varkappa_1$ and $\varkappa_2$. $[Fe]_t = 0.1051$ mC. Results: $\varkappa_1 = 14.0$; $\varkappa_2 = 0.32$.

h	b	$\frac{[RH]}{h}$	$\frac{(b-\varkappa')h}{[RH]}$
1.339	39.034	2.633	14.46
0.9845	54.732	3.578	14.90
0.7073	79.666	4.989	15.52
0.4556	131.75	7.733	16.47
0.2473	277.11	14.185	18.71
0.08714	1 141.4	39.706	26.86
0.04208	3 628.3	81.535	40.84
0.02421	9 307.7	140.975	59.83

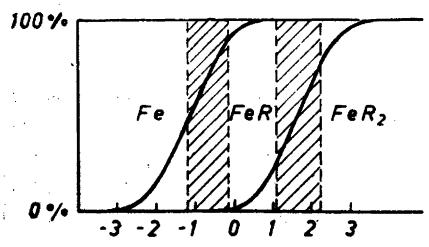


Fig. 4. Salicylamide. Distribution of Fe (III) *(in percent) over* Fe^{+3}, FeR^{+} *and* FeR_2^{-}, *as a function of* log [RH]/h.

Table 8. Salicylamide. Photometric determination of $\varkappa_1$. $[Fe]_t = [R]_t = 0.887$ mC.

h	Extinction at wave length							
	400	450	500	525	550	600	650	700
1.277	0.294	0.505	0.859	0.925	0.898	0.654	0.397	0.214
3.141	0.250	0.440	0.728	0.786	0.765	0.566	0.339	0.188
4.990	0.229	0.393	0.655	0.709	0.688	0.507	0.310	0.170
6.735	0.224	0.373	0.605	0.652	0.640	0.488	0.294	0.161
8.740	0.196	0.328	0.549	0.594	0.578	0.436	0.261	0.140
10.62	0.180	0.303	0.503	0.542	0.530	0.402	0.241	0.130
12.46	0.164	0.280	0.472	0.500	0.495	0.369	0.219	0.124
14.33	0.160	0.270	0.460	0.450	0.481	0.358	0.217	0.118

Table 9. Salicylamide. Photometric determination of $\varkappa_2$. $[Fe]_t = 0.199$ mC, $[R]_t = 3.54$ mC

h	Extinction at wave length							
	400	450	475	500	550	600	650	700
0.3430	0.117	0.220	0.290	0.336	0.318	0.212	0.110	0.060
0.2812	0.125	0.233	0.300	0.339	0.322	0.214	0.112	0.064
0.2116	0.131	0.250	0.318	0.362	0.330	0.212	0.115	0.060
0.1532	0.138	0.259	0.331	0.370	0.320	0.200	0.104	0.057
0.09493	0.162	0.310	0.380	0.410	0.338	0.199	0.094	0.046
0.04956	0.170	0.357	0.430	0.451	0.350	0.185	0.086	0.037
0.02659	0.210	0.412	0.480	0.485	0.351	0.170	0.070	0.030

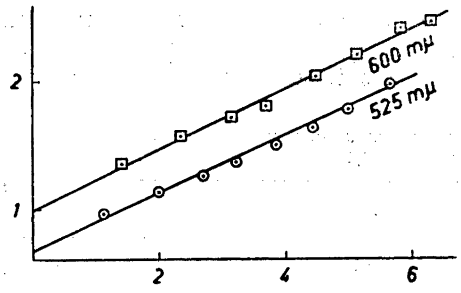


Fig. 5. Salicylamide. Photometric determination of $\varkappa_1$. c/E *vs.* $\sqrt{h/E}$. $c = [Fe]_t = [R]_t = 0.887$ mC.

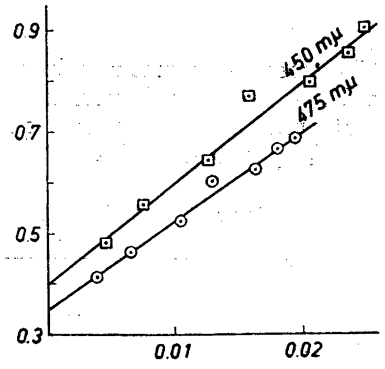


Fig. 6. Salicylamide. Photometric determination of $\varkappa_2$. $[Fe]_t/E$ *vs.* $\frac{h}{[RH]} \frac{E - \varepsilon_1 [Fe]_t}{E}$. $[Fe]_t = 0.199$ mC, $[R]_t = 3.54$ mC.

Table 10. Methyl salicylate. Potentiometric determination of $\varkappa_1$.
$[Fe]_t = 0.1032$ mC. Result: $\varkappa_1 = 0.36$ (mean value).

h	b	$\frac{[RH]}{h}$	$\frac{(b-\varkappa')h}{[RH]}$
1.627	1.3820	1.364	0.443
1.481	1.4669	1.498	0.393
1.403	1.5648	1.579	0.396
1.313	1.6770	1.687	0.387
1.182	1.8051	1.873	0.336
1.128	1.9277	1.962	0.345
1.060	2.0797	2.087	0.346
0.9845	2.2269	2.246	0.324
0.9226	2.3944	2.395	0.316

The present author [10] has determined the acidity constant of *o*-hydroxyacetophenone to be $1.5 \cdot 10^{-11}$ C, and thus their assumption must be wrong.

The solubility of *o*-hydroxyacetophenone is of the same order as that of salicylaldehyde. Thus the same restrictions have to be made here. No tendency to form the complex FeR_2 or higher complexes has been found.

The results of the potentiometric experiments are shown in Table 2 and 3. The calculated value of $\varkappa_1$ is given in Table 12. There is a remarkable difference in the results of these two experiments. However, this difference is not due to the formation of multinuclear complexes. If it were so, then the higher concentration of Fe would give a higher value of $\varkappa_1$. Instead the difference is due to the uncertainty in the results, owing to the influence of the OH-complexes on the measurements.

The photometric experiments are shown in Table 4 and Fig. 3. The calculated results are given in Table 12.

SALICYLAMIDE

The complex formation between iron(III)ion and salicylamide has been used by Hernández-Gutiérrez and Pulido-Cuchi [7] in a photometric method of determination of salicylamide. They suppose the complex to be $Fe(O \cdot C_6H_4 \cdot CONH_2)_6^{-3}$ and to be more stable than that of salicylic acid.

Table 11. Methyl salicylate. Photometric determination of $\varkappa_1$.
$[Fe]_t = 49.71$ mC, $[R]_t = 2.166$ mC.

h	Extinction at wave length							
	400	450	500	550	600	625	650	700
41.62	0.318	0.440	0.797	0.921	0.738	0.612	0.488	0.280
36.33	0.343	0.478	0.861	0.991	0.794	0.655	0.507	0.306
33.62	0.290	0.460	0.889	1.028	0.838	0.690	0.540	0.320
31.32	0.300	0.489	0.937	1.080	0.881	0.724	0.556	0.331
28.43	0.372	0.545	1.005	1.160	0.940	0.779	0.604	0.363
25.39	0.333	0.548	1.053	1.230	1.000	0.830	0.635	0.370

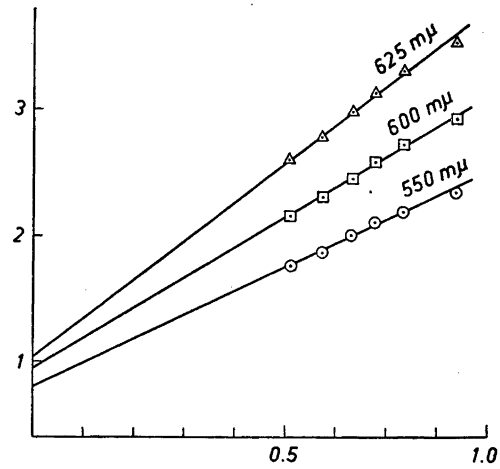


Fig. 7. Methyl salicylate. Photometric determination of $\varkappa_1$. $[R]_t/E$ *vs.* h/[Fe]. $[R]_t = 2.166$ mC, $[Fe]_t = 49.71$ mC.

Here the complex forming tendency is greater than that with either salicylaldehyde or *o*-hydroxyacetophenone, but the low solubility restricts the complex formation to FeR and FeR_2 only.

The results of the potentiometric experiments are shown in Tables 5—7, and the calculated values of $\varkappa_1$ and $\varkappa_2$ are given in Table 12.

Here the complex formation is so strong that both FeR and FeR_2 could be studied photometrically. From the potentiometrically calculated values of $\varkappa_1$ and $\varkappa_2$, Fig. 4 is constructed. From this figure, the suitable ranges of [RH]/h were chosen in which to make the photometrical experiments. These ranges are shadowed in the figure.

The results of the photometric determination of $\varkappa_1$ and ε_1 are shown in Table 8 and some of these results are used in calculating the curves of Fig. 5, equation (3) being used in the calculations. From the measurements on one of the most acidic solutions, ε_1 at other wave lengths could be calculated.

Table 12. Survey of the results of this investigation.

Substance	Potentiometry		Photometry					
	$\varkappa_1$	$\varkappa_2$	$\varkappa_1$	ε_1	$\lambda_{max.}$	$\varkappa_2$	ε_2	$\lambda_{max.}$
Salicylaldehyde	0.90 ± 0.05	$9.0 \cdot 10^{-3} \pm 0.5 \cdot 10^{-3}$	1.00 ± 0.05	1.2	550	—	—	—
o-Hydroxyacetophenone	0.5 ± 0.1	—	0.50 ± 0.05	1.3	550	—	—	—
Salicylamide	13.5 ± 0.5	0.3 ± 0.1	15.5 ± 1.0	1.5	525	0.40 ± 0.05	2.9	475
Methyl salicylate	0.35 ± 0.05	—	0.40 ± 0.05	1.2	550	—	—	—

In the same manner $\varkappa_2$ and ε_2 were calculated from some of the figures of Table 9, which resulted in the curves of Fig. 6. Here equation (5) was used. The results of the photometric determinations are collected in Table 12.

METHYL SALICYLATE

The complex formation with iron(III)ion was studied by Babko [8], using a photometric method. He found the complex FeR. The dissociation constant was determined $K = \frac{[R][Fe]}{[FeR]} = 4 \cdot 10^{-8}$C. This is twice the value of the corresponding constant of phenol. The difference, according to Babko, is due to methyl salicylate being a stronger acid.

The dissociation constant of the acid methyl salicylate was determined by Babko to $1.6 \cdot 10^{-8}$. This constant has been determined by Goldschmidt and Scholz [9] to be $1 \cdot 10^{-11}$. This author [10] has found the value $6.5 \cdot 10^{-11}$ in 3 000 mC ClO_4^-. The difference to Babkos value is striking. However, if the values found by Babko are used to calculate $\varkappa_1$, defined by this author, the value 0.4 is found, which is in good agreement with the results of this author.

In this work the results of a potentiometric titration are given in Table 10 and of the photometric determinations in Table 11 and Fig. 7. The constants calculated from these results are given in Table 12.

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