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INVESTIGATION OF COMPLEX FORMATION REACTIONS OF Fe(III) AND Al(III) WITH SOME PHENOL DERIVATIVES BY THE METHOD OF ION EXCHANGE*

By the method of ion exchange on the exchanger Dowex 50 WX 8 100-200 mesh complex formation was investigated in the system $Me(ClO_4)_3 + XC_6H_4OH + HClO_4 + NaClO_4 + H_2O$, with Me = Fe(III) or Al(III) and X = Cl, Br, CH_3, NO_2. It was proved that 1:1 complexes are formed between Me(III) and a phenol molecule. Stability constants of the complexes were determined and related with Hammett's sigma constants.

The great ability of phenol derivatives to form complexes with Fe(III) is well known. Spectrophotometric investigations [1] and studies of the kinetic isotope effect [2] showed, that within pH range 0.8-2.8, phenol and Fe(III) ion form a complex of the composition 1:1. Under such conditions phenol derivatives XC_6H_4OH are practically undissociated. The formation of the complex $[Fe(H_2O)_5(XC_6H_4O)]^{2+}$ is preceded by an intramolecular proton transfer [3-5] according to the formulas (1-3):

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \qquad (1)$$

$$[Fe(H_2O)_5(OH)]^{2+} + XC_6H_4OH \rightleftharpoons [Fe(H_2O)_4(OH)(HOC_6H_4X)]^{2+} + H_2O \qquad (2)$$

$$[Fe(H_2O)_4(OH)(HOC_6H_4X)]^{2+} \rightleftharpoons [Fe(H_2O)_5(OC_6H_4X)]^{2+} \qquad (3)$$

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[*] The work has been carried out within the research problem MR-I-14.

This mechanism has been confirmed for mono- and di-substituted phenols with the values $pK_a < 3$.

While investigating complexes of Fe(III) with some phenol derivatives Milburn [1] maintained constant ligand concentration equal to 0.05 M. This study used the method of ion exchange for widely varying ligand concentrations. Furthermore, investigations were carried out for a greater number of phenol derivatives (X = H, p-CH_3, p-Br, p-NO_2, m-NO_2, m-CH_3, m-Br, m-Cl) to be able to draw more general conclusions concerning the dependence of the complex stability on the ligand structure.

Complexes of phenol with Al(III) have not been investigated as yet, probably due to the complicated hydrolysis process. In aqueous solutions with pH < 3.00 Al(III) exists as a hexa-aquocomplex $[Al(H_2O)_6]^{3+}$. When pH = 3.00 in diluted solutions ($< 10^{-3}$ M) one distinguishes $[Al(OH)(H_2O)_5]^{2+}$ ions [6, 7], which are formed in a rapid and reversible reaction. It was to anticipate that this partly hydrolysed cation can form complexes with phenol, similarly as Fe(III).

Experimental

Reagents and solutions

The following materials were used in the investigations: cation exchanger Dowex 50 WX 8 100-200 mesh (The Dow. Chem. Co.), $Al(NO_3)_3$ and $Fe(NO_3)_3$ as starting salts, $HClO_4$, $NaClO_4$ (all from POCh-Gliwice) and substituted phenols XC_6H_4OH with X = p-CH_3, m-CH_3, m-NO_2, m-Br, m-Cl, p-Br, p-NO_2, H (BDH Poole). All reagents were pure for analysis.

Demineralized water with the specific conductance of 0.1-0.5 μS was used to prepare solutions.

Solutions of Fe(III) and Al(III) perchlorates were obtained acting with an exces of 30% $HClO_4$ on a freshly precipitated and washed deposit of hydroxides [8].

Methods

Complex formation reactions were investigated by the static method of ion exchange. Experiments were made in a glass reactor with the volume $V = 0.250\ dm^3$, containing 1×10^{-4} M solution of adequate metal perchlorate and a phenol derivative of a known concentration varying within the range of 1.5×10^{-5} M to 5.0×10^{-2}M.

For each solution the ionic strenght $\mu = 0.1$ and a defined pH value were maintained by adding the appropviate amounts of $NaClO_4$ and $HClO_4$ respectively. The solution was kept in a thermostat at the temperature of 293.0 ($\mp$ 0.1) K until the thermal equilibrium was reached. Then a weight portion (mass 0.250 g) of an air-dry cation exchanger in the hydrogen form was added. Both phases were separated after 3 h and the content of Me(III) in the solution was determined by 2,2'-dipyridyle method [9] and 8-hydroxyquinoline method [10] for Fe(III) and Al(III) respectively.

A Specol ZV photometer (K. Zeiss - Jena) was used to measure the absorbance. All the potentiometric measurements were made by means of a pH-meter OP -205 (Radelkis).

Results and discussion

The results of determining Me(III) concentration in solutions in equilibrium with cation exchanger allowed to calculate the numerical values of distribution coefficients D_M, for respective metal ions, which are given by the dependence (4):

$$D_M = \bar{C}_M / C_M \qquad (4)$$

where:

$\bar{C}_M$, C_M - are concentrations of metal ions in the resin phase and in the solution respectively.

The dependences of D_M on ligand concentration C_L are shown in Fig. 1 and 2 respectively for systems containing Fe(III) and Al(III).

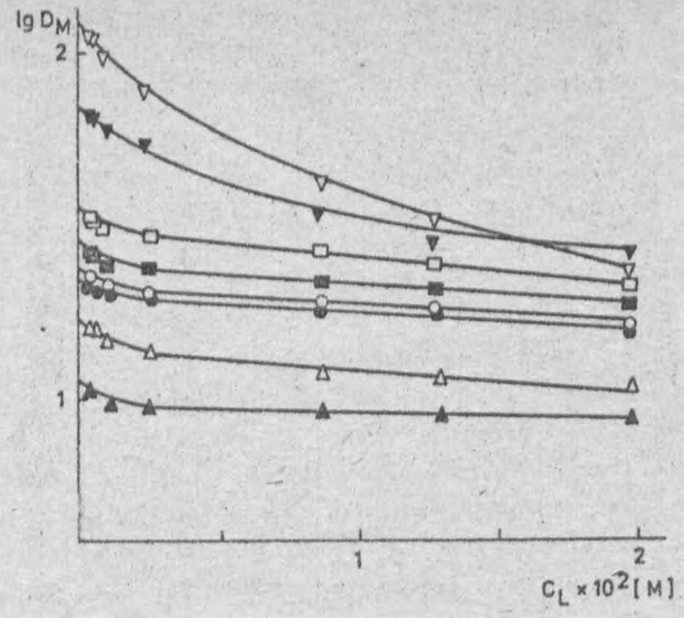

Fig. 1. Dependences of distribution coefficient of the metal D_M on the ligand concentration C_L for the system $Fe(ClO_4)_3$ + + $XC_6H_4OH + NaClO_4 + H_2O$, with X = p-$CH_3$ (▽), m-CH_3 (▼), m-NO_2 (□), m-Br (■), m-Cl (○), p-Br (●), p-NO_2 (△), H (▲). T = 293 K, $\mu = 0.1$, pH = 1.20

Limiting distribution coefficients D_o were determined by extrapolation of the function $D_M = f(C_L)$ to the value $C_L = 0$.

Stability constants β_n for complexes of Fe(III) and Al(III) were determined by Fronaeus method, using auxiliary functions: $F = f(C_L)$, $G = f(C_L)$ and $\Delta G(\Delta C_L)^{-1} = f[\Delta F(\Delta C_L)^{-1}]$ calculated from experimental D_M and D_o values [11]. The dependences $\Delta G(\Delta C_L)^{-1} = f[\Delta F(\Delta C_L)^{-1}]$ are shown in Fig. 3 and 4 respectively for systems containing Fe(III) (pH = 1.2) and Al(III) (pH = 3.1).

As seen from Fig. 3 functions $\Delta G(\Delta C_L)^{-1}$ reach 0 for the values $\Delta F(\Delta C_L)^{-1} = 0$ ($\beta_n = 0$ for $n > 1$), hence the formed Fe(III) complexes have the composition 1:1 and according to the previous works [2-4] are described by the formula $[Fe(H_2O)_5\, X_6H_4O]^{2+}$.

The same composition may be deduced from Fig. 4 for Al(III)

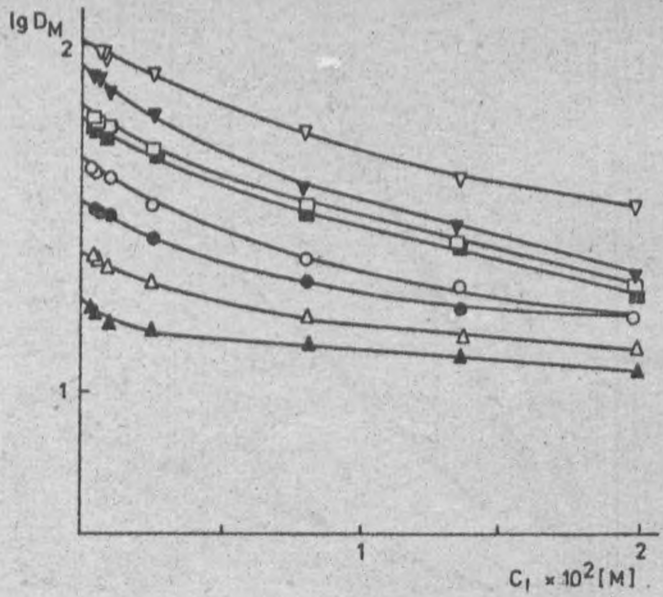

Fig. 2. The same dependences as in Fig. 1 for the system containing Al(III). T = 293 K, μ = 0.1, pH = 3.1

complexes formed at pH = 3.1 i. e. in solutions containing partially hydrolysed ions $[Al(OH)(H_2O)_5]^{2+}$. At pH < 3, when hydrolysis of Al^{3+} ion does not occur, complex formation was not revealed in the examined systems.

Equilibrium studies of ion exchange do not permit precise determination of the reaction mechanism, but basing on the previous investigations of systems with Fe(III) one can assume that the formation of Al(III) complexes runs as follows:

$$[Al(OH)(H_2O)_5]^{2+} + XC_6H_4OH \rightleftharpoons [Al(OH)(H_2O)_4(XC_6H_4OH)]^{2+} + H_2O \qquad (5)$$

$$[Al(OH)(H_2O)_4(XC_6H_4OH)]^{2+} \rightleftharpoons [Al(H_2O)_5(XC_6H_4O)]^{2+} \qquad (6)$$

Stability constants β_1 for the investigated metal complexes were determined from the slopes of the straight lines shown in Fig. 3 and 4. Numerical values of β_1 are summarized in Table 1.

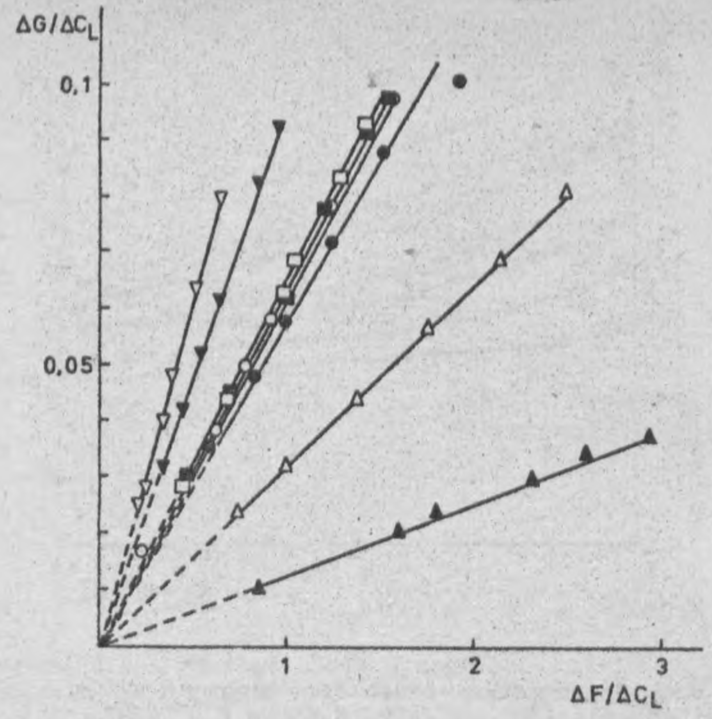

Fig. 3. Plots of Fronaeus auxiliary function $\Delta G\ (\Delta C_L)^{-1} = f[\Delta F\ (\Delta C_L)^{-1}]$ for the system $Fe(ClO_4)_3 + XC_6H_4OH + NaClO_4 + H_2O$, with X = p-$CH_3$ (▽), m-CH_3 (▼), m-NO_2 (□), m-Br (■), m-Cl (○), p-Br (●), p-NO_2 (△), H (▲)

Table 1

Numerical values of stability constants β_1 determined by Fronaeus method [11] for Fe(III) and Al(III) complexes with phenol derivatives (T = 293 K and $\mu = 0.1$)

Substituent X	Stability constants $\beta_1 \times 10^2$ for complexes $[Me(H_2O)_5\ XC_6H_4OH]^{2+}$	
	Fe(III)	Al(III)
p-CH_3	5.63 (∓0.12)	12.70 (∓0.57)
m-CH_3	3.91 (∓0.20)	9.82 (∓0.72)
m-NO_2	3.87 (∓0.11)	6.52 (∓0.18)

Table 1 (contd.)

Substituent X	Stability constants $\beta_1 \times 10^2$ for complexes $[Me(H_2O)_5(XC_6H_4OH)]^{2+}$	
	Fe(III)	Al(III)
m-Br	3.69 (∓0.15)	6.20 (∓0.21)
m-Cl	3.27 (∓0.22)	6.38 (∓0.63)
p-Br	3.25 (∓0.21)	5.76 (∓0.26)
p-NO_2	2.13 (∓0.13)	3.23 (∓0.33)
H	0.90 (∓0.10)	1.32 (∓0.20)

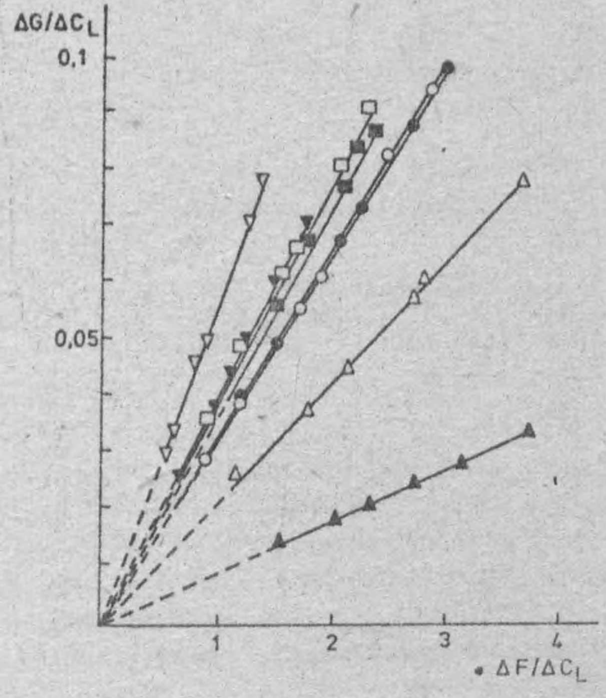

Fig. 4. The same plots as in Fig. 3 for the system containing Al(III)

It seems that Al(III) forms more stable complexes with phenols than Fe(III). It is particularly well seen for substituents being electron donors, e. g. $-CH_3$. The stability of complexes of both metal ions with nitro-substituted phenols is practically the same.

The determined stability constants β_1 may be related with the substituent position and type using Hammett's sigma constants [12]. The values of the ratio $\lg \beta_{1X}/\lg \beta_{1H}$ (where β_{1X} and β_{1H} are the constants for complexes with substituted and unsubstituted phenol respectively) for Fe(III) and Al(III) complexes are plotted against σ_X in Fig. 5.

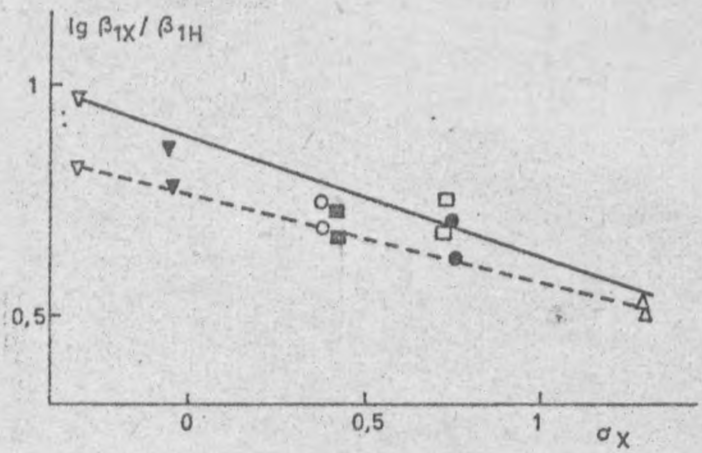

Fig. 5. Plots of the function $\lg \beta_{1X}/\beta_{1H}$ against Hammett's constants σ_X for the system $Me(ClO_4)_3 + HC_6H_4OH + NaClO_4 + H_2O$, with Me = Al(III) (—) and Fe(III) (---)

The slopes for the least squares lines, with standard deviations, are: $\varrho_{Al(III)} = -0.330$ (∓ 0.020) and $\varrho_{Fe(III)} = -0.238$ (∓ 0.012). Thus, the influence of the substituent position and type on complex stability is greater for Al(III) complexes than for Fe(III) ones. Substituents which decrease the acidity of phenol, increase the stability of complexes of both metals examined and the effect of substituents increasing the acidity of phenol is oposite.

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BADANIA REAKCJI KOMPLEKSOWANIA Fe(III) I Al(III) Z NIEKTÓRYMI POCHODNYMI FENOLU METODĄ WYMIANY JONOWEJ

Na podstawie badań wymiany jonowej w układach: $Me(ClO_4)_3$ + + $XC_6H_4OH + HClO_4 + NaClO_4 + H_2O$ + Dowex 50 W X 8 [Me = Fe(III) lub Al(III); X = Cl, Br, CH_3, NO_2] stwierdzono tworzenie się kompleksów o składzie Me:L = 1:1.

Oznaczenie stężeń Me (III) w roztworach będących w równowadze z kationitem pozwoliło obliczyć wartości liczbowe współczynników podziału metalu pomiędzy fazę roztworu i jonitu (D_M i D_o). Na podstawie eksperymentalnie wyznaczonych D_M i

D_o, stosując metodę Fronaeusa obliczono stałe trwałości β_1. Stałe trwałości β_1 skorelowano z położeniem i rodzajem podstawnika stosując równanie Hammetta. Wartości stałych ϱ wynoszą dla Al (III) $\varrho = -0,330$ (+0,020), a dla Fe (III) $\varrho = -0,238$ ($\pm 0,012$). Zatem wpływ położenia i rodzaju podstawnika jest większy dla kompleksów Al (III) niż dla kompleksów Fe (III). Podstawniki, które zmniejszają kwasowość fenolu zwiększają stabilność kompleksów obydwu badanych metali, a wpływ podstawników zwiększających kwasowość fenolu jest odwrotny.

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ИССЛЕДОВАНИЕ РЕАКЦИИ КОМПЛЕКСООБРАЗОВАНИЯ Fe(III) И Al(III) ИЗ НЕКОТОРЫМИ ПРОИЗВОДНЫМИ ФЕНОЛА МЕТОДОМ ИОННОГО ОБМЕНА

Методом ионного обмена на сильнокислой смоле Dowex 50 W X 8 исследованы реакции комплексообразования в системах: [$Me(ClO_4)_3 + XC_6H_4OH + HClO_4 + NaClO_4 + H_2O$ [Me = Fe(III) либо Al(III); X = = Cl, Br, CH_3, NO_2]. Установлено образование комплексов состав которых соответствует соотношению Me(III): L = 1 : 1. Определено константы стойкости и их зависимости параметров Гамметта.