

EXTRACTION OF IRON(III) FROM THE CITRIC MEDIUM
BY THE TOLUENE SOLUTION OF TRILAURYLAMINE

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The composition of Fe(III) complexes extracted from the aqueous phase of constant ionic strength ($1M-(H_3,Na_3,Fe)A$, where H_3A denotes citric acid) by the toluene solution of trilaurylamine (TLA) has been determined and the respective extraction constants have been calculated. In the concentration range $c_{Fe} < 10^{-2} \text{ mol l}^{-1}$ $FeA(TLA)_2$ and $FeA(TLA)_4(H_3A)_{2-4}$ are the predominant complexes in the organic phase. The abundance of the $(FeA)_3(TLA)_6(H_3A)_2$ complex in the organic phase increases at higher equilibrium concentrations of Fe(III) in the aqueous phase and at higher concentrations of TLA.

Metal cations can be extracted by alifatic amines in the form of complexes with organic acids. A systematic survey of the extraction properties of systems formed by amines of all 4 classes and by various acids (dicarboxylic acids, hydroxy acids, and aminopolycarboxylic acids) has been published by Moore¹. A number of them is exploited in analytical chemistry² but only little attention has been paid to the composition of the extracted complexes.

The most detailed studies have been published on the stoichiometry of the extraction of metal chelates of aminopolycarboxylic acids by quarternary ammonium salts^{3,4}, the extraction of oxalates by tertiary amines⁵, and the extraction of metals from the solutions of various carboxylic and substituted carboxylic acids by tertiary amines^{6,7} as well as in systems similar to the system under study. The logarithmic analysis of the experimental data obtained in the extraction of Fe(III) by trioctylamine (TOA) from the citric acid (H_3A) medium revealed^{6,7} that $FeA(TOA)_4 \cdot (H_3A)_2$ is the predominant complex in the organic phase.

The description of organic complexes in this study is based on the results of our previous papers in which the composition of the citric acid complexes with trilaurylamine⁸ (TLA) as well as the composition of Fe(III) citrate complexes in the $1M-(H_3,Na_3,Fe)A$ medium⁹ (which is also used in this study) have been determined. The constant ionic strength cannot be maintained using salts of strong mineral acids because the bond of the alkylammonium cation with the mineral acid anion is stronger than that with the organid acid anion or with the anionic complex of the metal with a weak organic acid ligand so that the mineral anion displaces the anion of the organic acid in the alkylammonium salt and releases it into the aqueous phase. Due to the

incomplete dissociation of H_3A the $1M-(H_3,Na_3,Fe)A$ solution cannot be taken for a solution of constant ionic strength but the results obtained in the citric acid extractions⁸ show that the activity coefficients of the components in this solution remain approximately constant. The constant value of the ionic strength is obviously more affected by changes of the hydrogen ion concentration than by the changes of the concentration of iron.

EXPERIMENTAL

Reagents and Solutions

Trilaurylamine ("pureté nucléaire", Rhône-Poulenc), toluene, citric acid, sodium citrate (all of the analytical grade, Lachema), and Fe(III) citrate (pure, Lachema) were used without further purification. The content of tertiary amines in TLA was determined by the method published elsewhere⁸. The toluene solutions of TLA were prepared by weighing and their concentrations are given relatively to the content of tertiary amines. Solutions of the concentrations of 0.0302, 0.0783, 0.155, and 0.308 mol l⁻¹ i.e. 5, 10, 20 vol. % were used. The aqueous solutions for the extraction were prepared from the stock solution of 0.4 mol l⁻¹ of Fe(III) and 1 mol l⁻¹ of H_3A . The content of iron in this solution was determined as thiocyanate by a below-described spectrophotometric method, the content of free H_3A was determined by the potentiometric titration with the Fe(III) solution using the method of Šúcha and Volka¹⁰.

Procedures

Extractions. The solutions were extracted by the same procedure as in the studies of the citric acid extractions⁸ except that the shaking time was prolonged to 5 h. After the separation of the two phases the concentrations of iron and H_3A in both phases were determined and the pH value of the aqueous phase was measured.

Determination of iron in the aqueous phase. 2 ml of concentrated HCl, 15 ml of acetone and water are added to the aqueous phase sample (≤ 5 ml) so that the total volume is 20–22 ml. After adding 2 ml of 4M-KSCN the volume is made up with water to 25 ml. The absorbance at the wavelength of 480 nm is measured after 5–15 min. Under these precautions the presence of citrates up to the concentration of 0.2 mol l⁻¹ in the final solution does not decrease the absorbance by more than 3%. The error increases with the decrease of acidity or with the decrease of the acetone concentration.

Determination of iron in the organic phase. 5 ml of the thiocyanate reagent are added to the organic phase dissolved in 3 ml of toluene and the solution is made up to 10 ml with ethanol. The absorbance at the wavelength of 480 nm is measured after 10–30 min. A calibration curve must be measured with solutions containing the same amount of TLA as the measured samples because the presence of TLA increases the absorbance by <30%. The samples had to be either diluted to the extent when the effect of TLA was negligible (<0.5 vol.% of TLA in the measured solution), or, in samples with a lower concentration of iron that could not be diluted further, TLA concentration was adjusted to a value for which the calibration curve had been measured. Citric acid contained in 3 ml of the organic phase does not interfere in the determination. The thiocyanate reagent is prepared by the dissolution of 5 g of potassium thiocyanate in 100 ml of 96% ethanol, by adding 5 ml of concentrated HCl, by filtration, and by adding 2.5 ml of water to the filtrate. The reagent is stable for 24 h.

The error of the iron concentration determination by these methods did not exceed 1–3%. The deviation of the mass balance of iron in both phases from the initial mass was maximum 5% and mostly it was better than 2%.

Citric acid from the organic phase was reextracted by the solution of 8M-HCl (in this case iron remains in the organic phase) or by the solution of 0.4M-HClO₄ + 2M-NaClO₄ (iron is extracted into the aqueous phase) and its content was determined by the potentiometric titration with the FeCl₃ solution¹⁰. In the reextraction by 8M-HCl relatively large volume changes were observed (the volume of the aqueous phase increases by 3% if 20% TLA is used) so that corresponding corrections should be made. The reextraction yield was >97%. Using NaClO₄ + HClO₄ solution the reextraction yield was higher than 99% and the volume increased by maximum 1%. Because iron is reextracted simultaneously, the titration determines the difference between the concentrations of citric acid and iron in the organic phase. The concentration of citrates in the aqueous phase as calculated from the mass balance was within the limits $1 \pm 0.03 \text{ mol l}^{-1}$.

The measurement of the hydrogen ion concentration in the aqueous phase and the calibration of the glass electrode in the citrate medium was made as it was described in our previous paper⁹.

Extraction and all subsequent measurements were done at the temperature of $25.0 \pm 0.5^\circ\text{C}$.

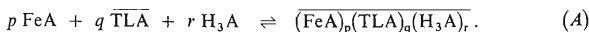
RESULTS

For all concentrations of TLA (c_{TLA}) the dependence of the extraction of Fe and H₃A on the equilibrium concentration of Fe in the aqueous phase ($c_{\text{Fe,aq}}$) has been measured and expressed in terms of the functions $Z_{\text{Fe}} = f(c_{\text{Fe,aq}})$ and $Z_{\text{A}} = f(c_{\text{Fe,aq}})$, where $Z_{\text{Fe}} = c_{\text{Fe,org}}/c_{\text{TLA}}$ and $Z_{\text{A}} = c_{\text{H}_3\text{A,org}}/c_{\text{TLA}}$ as well as the dependence of Fe extraction on pH, $D_{\text{Fe}} = f(\text{pH})$, where D_{Fe} is the distribution ratio of Fe and the symbols c denote the respective analytical concentrations. The dependences $Z_{\text{Fe}} = f(c_{\text{Fe,aq}})$ and $Z_{\text{A}} = f(c_{\text{Fe,aq}})$ were measured at $\text{pH} = 2.87 \pm 0.03$ (Table I, Figs 1 and 2). At this pH value the buffer capacity is already high enough and at the same time hydrolysis of the citrate complexes of iron does not take place.

The dependence $D_{\text{Fe}} = f(\text{pH})$ (Table II, Fig. 3) was measured at $c_{\text{Fe,aq}} < 10^{-4} \text{ mol l}^{-1}$. Under these conditions the distribution ratio of iron is independent of its concentration. The pH range was 3.1–1.8. At $\text{pH} > 3.1$ hydrolytic complexes are formed in the aqueous phase⁹ while at acidities higher than $\text{pH} 1.8$ the separation of both phases is difficult and the reproducibility of results is poor.

Data Processing

Due to the non-polar character of toluene as the organic phase solvent only uncharged species can be assumed to exist in the organic phase. The extraction of Fe(III) from the citrate medium can therefore be formally described as a reaction of the complex FeA with H₃A and TLA,



The components of the organic phase are denoted by a bar.

Assuming the adopted method of maintaining the constant ionic strength of the medium as sufficient so that the activity coefficients of all components can be assumed to be constant in the whole concentration range under study, the equilibrium

TABLE I

Extraction of Fe(III) by the Toluene Solutions of TLA from 1M-(H₃,Na₃,Fe)A Solutions at a Constant pH Value of the Equilibrium Aqueous Phase

The values of log $c_{Fe,aq}$, pH, Z_{Fe} , and Z_A are given for every point.

0.0302M-TLA			
-4.599, 2.875, 0.000626, 0.245;	-4.114, 2.863, 0.00173, 0.243;		
-3.796, 2.863, 0.00331, 0.244;	-3.378, 2.846, 0.00728, 0.248;		
-3.070, 2.845, 0.0118, 0.237;	-2.764, 2.854, 0.0215, 0.247;		
-2.435, 2.853, 0.0338, 0.274;	-2.016, 2.858, 0.0632, 0.278;		
-1.697, 2.869, 0.0993, 0.287;	-1.100, 2.882, 0.181, 0.377;		
-0.916, 2.853, 0.215, 0.417;			
0.0783M-TLA			
-4.484, 2.893, 0.00128, 0.424;	-4.203, 2.887, 0.00250, 0.423;		
-3.788, 2.867, 0.00610, 0.429;	-3.370, 2.875, 0.0116, 0.414;		
-3.126, 2.871, 0.0214, 0.424;	-2.780, 2.873, 0.0397, 0.425;		
-2.440, 2.860, 0.0749, 0.444;	-1.947, 2.867, 0.144, 0.483;		
-1.728, 2.860, 0.182, 0.492;	-1.609, 2.883, 0.212, 0.511;		
-1.218, 2.868, 0.286, 0.536;	-1.009, 2.863, 0.333, 0.601;		
0.155M-TLA			
-4.484, 2.881, 0.00145, 0.577;	-4.088, 2.878, 0.00362, 0.579;		
-3.772, 2.874, 0.00698, 0.569;	-3.313, 2.868, 0.0175, 0.563;		
-2.967, 2.870, 0.0340, 0.563;	-2.644, 2.855, 0.0641, 0.576;		
-2.294, 2.896, 0.116, 0.582;	-1.752, 2.895, 0.228, 0.623;		
-1.455, 2.862, 0.298, 0.653;	-1.156, 2.887, 0.355, 0.656;		
-1.023, 2.887, 0.371, 0.679;	-0.959, 2.839, 0.402, 0.705;		
0.308M-TLA			
-4.136, 2.874, 0.00192, 0.663;	-3.983, 2.866, 0.00371, 0.663;		
-3.646, 2.874, 0.00735, 0.660;	-3.346, 2.877, 0.0137, 0.670;		
-2.900, 2.874, 0.0359, 0.662;	-2.606, 2.877, 0.0665, 0.696;		
-2.236, 2.892, 0.143, 0.712;	-1.900, 2.890, 0.229, 0.693;		
-1.547, 2.873, 0.320, 0.745;	-1.279, 2.857, 0.355, 0.748;		
-1.031, 2.827, 0.408, 0.761;	-1.045, 2.859, 0.408, 0.764;		

constant of the reaction (A) can be written as

$$\beta_{p,q,r} = \frac{[(\text{FeA})_p(\text{TLA})_q(\text{H}_3\text{A})_r]}{[\text{FeA}]^p[\text{TLA}]^q[\text{H}_3\text{A}]^r} \quad (1)$$

At first the relations between the coefficients p , q , and r were determined. then all the complexes corresponding to these relations were listed and from this list a set of complexes was chosen which fulfils best the experimental data. In this procedure the following computational programs were used:

MESAK¹¹. It determines the function $\bar{q} = f(\bar{p})$ from the data $Z = f(\log a)_B$, where a is the concentration of the free component A, B is the total concentration

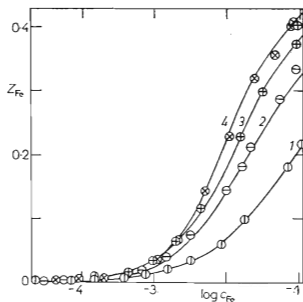


FIG. 1

Dependence of Z_{Fe} on $\log c_{\text{Fe, aq}}$ for the Extraction of Iron by the Toluene Solution of TLA from 1M-(H₃,Na₃,Fe)A at pH 2.87 1 2% TLA, 2 5% TLA, 3 10% TLA, 4 20% TLA

The solid curves were calculated using the following extraction constants of the metal $\log \beta_{1,2,0} = 3.89$, $\log \beta_{1,4,2} = 8.36$, $\log \beta_{2,4,0} = 10.68$, $\log \beta_{2,5,1} = 12.56$, $\log \beta_{3,6,2} = 18.32$, and $\log \beta_{3,6,3} = 18.64$ and the following extraction constants of H₃A $\log \beta_{0,2,1} = 1.30$, $\log \beta_{0,3,2} = 3.05$, $\log \beta_{0,3,3} = 3.05$, and $\log \beta_{0,6,5} = 8.66$.

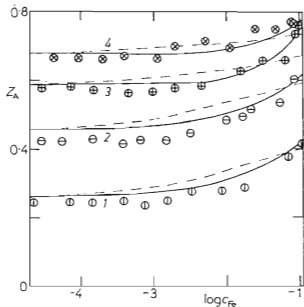


FIG. 2

Dependence of Z_A on $\log c_{\text{Fe, aq}}$ for the Extraction of Iron by the Toluene Solutions of TLA from 1M-(H₃,Na₃,Fe)A at pH 2.87

1 2% TLA, 2 5% TLA, 3 10% TLA, 4 20% TLA. The solid curves were calculated for the first set of complexes (*i.e.*, (1,2,0), (1,4,2), (2,4,0), (2,5,1), (3,6,2), and (3,6,3)) and the dashed curves for the second set of complexes (*i.e.*, (1,2,0), (1,4,2), (2,4,0), (2,5,1), (3,6,2), and (1,4,4)) as given in Table III. The used extraction constants of H₃A are given in Fig. 1, the extraction constants of Fe in Table III.

of the component B, \bar{q} and \bar{p} are the mean values of the coefficients of the complex A_pB_q . This program is based on the differential relations derived by Sillén¹².

TABLE II

Dependence of the Distribution Ratios of Fe(III) on pH of the Aqueous Phase in the Extraction by Toluene Solutions of TLA from 1M-(H₃,Na₃,Fe)A

The values of pH, log $c_{Fe,aq}$, and log D_{Fe} are given for every point.

0.0302M-TLA

3.087, -4.424, -0.454; 2.875, -4.599, -0.125; 2.644, -4.469, 0.188; 2.386, -4.398, 0.509, 2.380, -3.991, 0.487; 2.385, -3.635, 0.436; 2.381, -3.221, 0.403; 2.046, -4.317, 0.886; 1.764, -4.181, 1.076;

0.0783M-TLA

3.049, -4.516, 0.303; 2.893, -4.484, 0.484; 2.620, -4.533, 0.892; 2.398, -4.541, 1.138; 2.052, -4.517, 1.424; 1.757, -4.452, 1.679;

0.155M-TLA

3.082, -4.533, 0.693; 2.881, -4.484, 0.835; 2.644, -4.544, 1.132; 2.398, -4.510, 1.422; 2.041, -4.439, 1.757; 1.763, -4.343, 1.964;

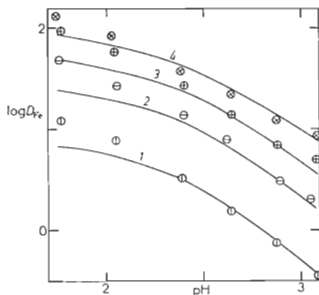
0.308M-TLA

3.083, -4.583, 0.936; 2.874, -4.316, 1.087; 2.640, -4.433, 1.339; 2.380, -4.244, 1.574; 2.384, -3.936, 1.550; 2.376, -3.652, 1.577; 2.026, -4.317, 1.925; 1.739, -4.503, 2.114;

FIG. 3

Dependence of the Distribution Ratio of Fe(III) on the pH Value of the Equilibrium Aqueous Phase for the Extraction in the System 1M-(H₃,Na₃,Fe)A-TLA-Toluene

1 2% TLA, 2 5% TLA, 3 10% TLA, 4 20% TLA. The solid curves were calculated using the equilibrium constants for the second set of complexes (*i.e.*, (1,2,0), (1,4,2), (2,4,0), (2,5,1), (3,6,2), and (1,4,4)) as given in Table III.



HALTAFALL¹³. Using the given equilibrium constants $\beta_{p,q,r}$ the concentrations of the complexes $A_pB_qC_r$ are calculated for the desired values of c_A , c_B , and c_C . The values of free concentrations of the components A, B, and C that are necessary for the computation are determined in the program by a successive approximation.

LETAGROP¹⁴. It chooses the best set of complexes $A_pB_qC_r$ from the given list and it determines the values of $\beta_{p,q,r}$, corresponding to the minimum of the function

$$U = \sum (f(y_{exp} - y_{calc}))^2, \quad (2)$$

where y is the measured quantity.

Determination of p, q, r Values

The method used in the program MESAK can calculate only the coefficients of a complex formed by two components. Therefore only pairs of coefficients were determined for sets of data with a constant concentration of the third component. In principle the program MESAK can also be used for the sets of data obtained at constant pH value. In this program for two-component complexes the auxiliary variables are

$$S = \sum [A_pB_q], \quad \text{and} \quad (3)$$

$$R = (S + b)/B. \quad (4)$$

Here and in the subsequent text the capital letters (A, B, C) denote the total concentrations and the small letters (a, b, c) the free concentrations of the individual components from which the complex is formed.

The variables S and R have the same form even for a three-component system at a constant concentration of one of the components as can be proved by this reasoning¹²: the differential of Eq. (3) is

$$dS = (A - a) d \ln a + (B - b) d \ln b \quad (5)$$

and the analogous expression for the three-component system is

$$dS = (A - a) d \ln a + (B - b) d \ln b + (C - c) d \ln c. \quad (6)$$

However, for $c = \text{const}$, Eq. (6) becomes Eq. (5) so that the variables S and R are identical for both these systems.

The integration constants that must be specified in the input data for the computation with the program MESAK were calculated in points where $Z = 0$ using the extraction constants of citric acid in the system $1M-(H_3, Na_3)A$ -TLA-toluene.

The execution of the program MESAK presents the values \bar{p} and \bar{q} corresponding to all species present in the organic phase so that they include also complexes of H_3A with the amine. However, the interpretation of these values would be difficult. If the equilibrium constants of some complexes appearing in the system under study are known, then these complexes can be eliminated from the computation and the values found for \bar{p} and \bar{q} include only the remaining complexes. In our case the correction has been made for the presence of the complexes $(TLA)_q(H_3A)_r$, the extraction constants $\beta_{0,q,r}$ of which were determined in our previous paper⁸ so that the computed values \bar{p} and \bar{q} correspond only to the complexes $(FeA)_p(TLA)_q(H_3A)_r$.

Moreover, the dependence $(\bar{p} + \bar{r}) = f(\bar{q})$ has been calculated using the mass balance

$$\bar{p} + \bar{r} = \bar{p}((Z_A - \sum r\beta_{0,q,r}b^q c^{r/B})/Z_{Fe}). \quad (7)$$

The dependences $\bar{q} = f(\bar{p})$ and $(\bar{p} + \bar{r}) = f(\bar{q})$ for $Z_{Fe} \geq 0.1Z_A$ are presented in Figs 4 and 5.

For the data measured at low concentrations of Fe the following simplification has been made: If the distribution ratio of the complex FeA is defined as $D_{FeA} = c_{Fe,org}/[FeA]_{aq}$ then

$$D_{FeA} = \text{const. } \bar{p}a^{\bar{p}-1}b^{\bar{q}}c^{\bar{r}}, \quad (8)$$

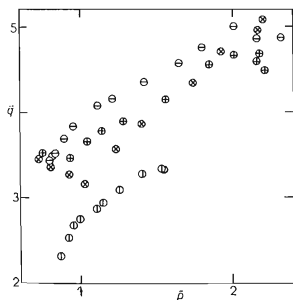


FIG. 4

Dependence of \bar{q} on \bar{p} for the Complexes $(FeA)_p(TLA)_q(H_3A)_r$ Formed in the Organic Phase During the Extraction in the System $1M-(H_3,Na_3,Fe)A-TLA-Toluene$ at pH 2.87

○ 2% TLA, □ 5% TLA, △ 10% TLA, ⊗ 20% TLA.

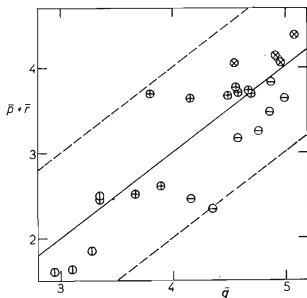


FIG. 5

Dependence of $(\bar{p} + \bar{r})$ on \bar{q} for the Complexes $(FeA)_p(TLA)_q(H_3A)_r$ Formed in the Organic Phase During the Extraction in the System $1M-(H_3,Na_3,Fe)A-TLA-Toluene$ at pH 2.87

○ 2% TLA, □ 5% TLA, △ 10% TLA, ⊗ 20% TLA.

where $a = [\text{FeA}]$, $b = [\overline{\text{TLA}}]$, and $c = [\text{H}_3\text{A}]$ (the value for $[\text{FeA}]$ is calculated for every point using the equilibrium constants of the citrate complexes of Fe (ref.⁹) and the protonation constants of citric acid⁸). Because at low iron concentrations the distribution coefficient is independent of c_{Fe} (and therefore also of $[\text{FeA}]$) it can be assumed that in this range of c_{Fe} only mononuclear complexes (relatively to FeA) are formed so that $p = 1$ and Eq. (8) becomes

$$D_{\text{FeA}} = \text{const. } b^{\bar{q}} c^{\bar{r}}. \quad (9)$$

The average composition of complexes in the region where $c_{\text{Fe}} \leq 10^{-4}\text{M}$ can therefore be determined by the logarithmic analysis using the following expressions:

$$\bar{q} = (\partial \log D_{\text{FeA}} / \partial \log b)_{\log c}, \quad \text{and} \quad (10)$$

$$\bar{r} = (\partial \log D_{\text{FeA}} / \partial \log c)_{\log b}. \quad (11)$$

In our case the value of the derivative $(\partial \log D_{\text{FeA}} / \partial \log c)_{\log b}$ could not be found directly in the whole concentration range and therefore the following transformation had to be used

$$\begin{aligned} \bar{r} &= -(\partial \log D_{\text{FeA}} / \partial \log b)_{\log c} \cdot (\partial \log b / \partial \log c)_{\log D_{\text{FeA}}} = \\ &= -\bar{q} (\partial \log b / \partial \log c)_{\log D_{\text{FeA}}}. \end{aligned} \quad (12)$$

The unknown free concentration of TLA was calculated by the program HALTAFALL using the known values of $\log a$, B (= the total concentration of TLA in the organic phase), and the equilibrium constants of the citric acid extraction determined in our previous study⁸.

In the region of low Z_{Fe} ($Z_{\text{Fe}} \rightarrow 0$) the values $\bar{q} = 3-4$ and $\bar{p} = \bar{q} - 1$ have been found.

From Fig. 4 it can be deduced that mononuclear complexes (relatively to iron) containing 2-4 molecules of amine are transformed into polynuclear complexes as the concentration of iron in the aqueous phase increases and \bar{p} acquires the values > 2 and $\bar{q} > 5$. The value of the coefficient \bar{r} can be estimated from Fig. 5, from which it follows that for $Z > 0.1$ $\bar{q} - (\bar{r} + \bar{p}) = 1 \pm 1$, and also from the results for $Z \rightarrow 0$, where $\bar{r} = \bar{q} - 1$.

In the following text the complexes $(\text{FeA})_p(\text{TLA})_q(\text{H}_3\text{A})_r$ will be for simplicity written as (p, q, r) . The points in Figs 4 and 5 are rather scattered, similarly as in other extraction systems with trialkylamines¹⁵ which can be ascribed to the fact that the above-mentioned conditions under which the three-component system can be reduced to a two-component system were not completely fulfilled and also to the fact that

the nature of the bond in the alkylammonium salts tends to the formation of a series of complexes rather than to the formation of a low number of discrete species. Therefore, as the first approximation, all the complexes lying in the region of values given by the points in Figs 4 and 5 and also in the region obtained by extrapolation to higher values of \bar{p} and \bar{q} , were taken into consideration. The best set of complexes was chosen by the program LETAGROP using the selector of complexes¹⁶. The sum of squares of the absolute values of relative errors

$$U = \sum \{ \text{abs} [(Z_{\text{Fe,calc}} - Z_{\text{Fe,exp}})/Z_{\text{Fe,calc}}] + \text{abs} [(Z_{\text{A,calc}} - Z_{\text{A,exp}})/Z_{\text{A,calc}}] \}^2 \quad (13)$$

has been minimized.

At first the calculation was executed for the points with constant pH value (Table I). These data are best fitted with the set of complexes (1,2,0), (1,4,2), (2,4,0), (2,5,1), (3,6,2), and (3,6,3), the stability constants of which are given in Table III. A fit of the theoretical curves $Z_{\text{Fe}} = f(\log c_{\text{Fe,aq}})$ and $Z_{\text{A}} = f(\log c_{\text{Fe,aq}})$ calculated from these constants to the experimental data is given in Figs 1 and 2. A good agreement was obtained for the extraction of Fe, *i.e.*, for the values Z_{Fe} , while for the values of Z_{A} a systematic positive deviation is observed in the region of low concentrations of Fe and amine. Because this deviation is found even at such concentrations of Fe at which only a negligible amount of citrates in the organic phase is bound into a complex with Fe it can be assumed that the main reason for this deviation is probably in the change of the values of extraction constants of citric acid itself caused by the change of the $1\text{M}-(\text{H}_3, \text{Na}_3)\text{A}$ ionic medium into $1\text{M}-(\text{H}_3, \text{Na}_3, \text{Fe})\text{A}$.

Including into the calculation — along with the series of results at constant pH value — also other points with low Z in the pH region 2.3–3.1 (Table II) a reasonable agreement with the experimental points can be achieved only under the assumption that the formation of the complex (1,4,4), which represents complexes with a higher ratio $\text{H}_3\text{A} : \text{TLA}$, is taken into consideration and the complex (3,6,3) is not present. The respective stability constants are also given in Table III. The theoretical extraction curves calculated with these constants are presented in Fig. 3. These curves deviate from the experimental data in the region of $\text{pH} < 2.1$ but these systematic deviations were not analyzed.

DISCUSSION

The stoichiometric composition of a part of the complexes in both sets given in Table III corresponds, at least from the formal point of view, to the general type of complexes as they were found for the salts of H_3A with TLA in our previous work⁸. Using the symbolism adopted in this work the complexes of H_3A with TLA have

the composition $(0, q, r)$ and the coefficients q and r are related by the relation $r = q + 1$. A similar relation is valid also for certain complexes of iron assuming that the species FeA and H_3A are equivalent from the point of view of the bond in the complex $(\text{FeA})_p(\text{TLA})_q(\text{H}_3\text{A})_r$. The relation $(p + r) = q + 1$ is then fulfilled in the complexes $(1, 2, 0)$, $(1, 4, 2)$, and $(3, 6, 2)$ so that it can be assumed that they are formed from the respective complexes of H_3A with TLA by the ion exchange.

The composition of some of the remaining complexes is rather close to this relation between the coefficients p , q , and r (complexes $(2, 4, 0)$ and $(2, 5, 1)$) but the composition of the complexes $(3, 6, 3)$ and $(1, 4, 4)$ is substantially different. A question therefore appears in what extent the two latter complexes represent the actual species existing in the solution.

As it was already discussed in the previous papers^{8,9} the adopted method of maintaining the constant ionic medium does not ensure a constant ionic strength and thus also the constant values of the activity coefficients of individual components in the whole region under study.

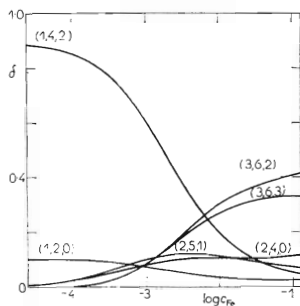
Another error may appear when the extraction constants of the complexes of H_3A with TLA determined for the aqueous phase $1\text{M}-(\text{H}_3, \text{Na}_3)\text{A}$ are used in the system $1\text{M}-(\text{H}_3, \text{Na}_3, \text{Fe})\text{A}$. This seems, *e.g.*, to be indicated by Fig. 2 in which the experimental points are compared with the curves calculated for the obtained set of complexes.

TABLE III

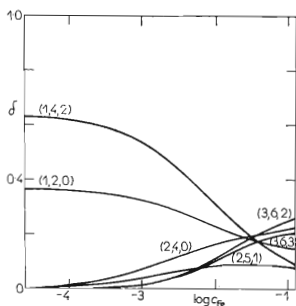
Various Models of the Description of Fe(III) and H_3A Extraction in the System $1\text{M}-(\text{H}_3, \text{Na}_3, \text{Fe})\text{A}$ -TLA-Toluene

Model	Logarithm of the equilibrium constant of the complex ^a	U	No of points
$(1, 2, 0)$; $(1, 4, 2)$; $(2, 4, 0)$; $(2, 5, 1)$; $(3, 6, 2)$; $(3, 6, 3)$	3.89 ± 0.18 ; 8.36 ± 0.07 ; 10.68 max 11.01 ; 12.56 ± 0.04 18.32 max 18.56 ; 18.64 ± 0.02	0.453	47
$(1, 2, 0)$; $(1, 4, 2)$; $(2, 4, 0)$; $(2, 5, 1)$; $(3, 6, 2)$; $(1, 4, 4)$	3.79 max 4.01 ; 7.97 ± 0.14 10.82 max 11.16 ; 12.51 max 12.96 18.56 ± 0.22 ; 8.94 ± 0.02	1.142	65

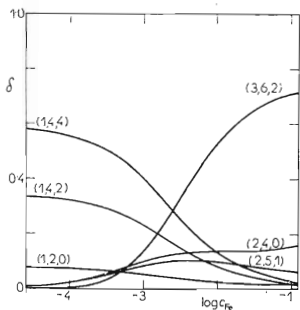
^a The precision of the calculated constants is given as $\pm 3s(\beta)$, where $s(\beta)$ is the mean standard deviation of β that is obtained by the program LETAGROP. The reliability interval of the constant $\beta \pm 3s(\beta)$ is transformed to the logarithmic scale using the approximate relation $\log \beta \pm \pm (\log(\beta + 1.5s(\beta)) - \log(\beta - 1.5s(\beta)))$ (ref.¹⁸). If $s(\beta) > 0.2\beta$ this relation is not correct and only the upper limit of the deviation, *i.e.*, $\log(\beta + 3s(\beta))$ is given and it is denoted β max $(\beta + 3s(\beta))$.



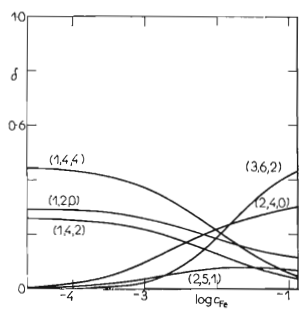
a



a



b



b

FIG. 6

Dependence of the Ratio of Individual Complexes of Fe in the Organic Phase to the Total Concentration of Fe in the Organic Phase (δ) on the Equilibrium Concentration of Fe in the Aqueous Phase (c_{Fe}) in the Extraction by 0.3075M Solution of TLA in Toluene from 1M-(H₃,Na₃,Fe)A at pH 2.87

The complexes $(FeA)_p(TLA)_q(H_3A)_r$ are denoted by the symbols (p,q,r) , $\delta = p[(p,q,r)]$: $\sum p[(p,q,r)]$ was calculated using the extraction constants given in Table III; a for the set (1,2,0), (1,4,2), (2,4,0), (2,5,1), (3,6,2), (3,6,3); b for the set (1,2,0), (1,4,2), (2,4,0), (2,5,1), (3,6,2), (1,4,4).

FIG. 7

The Same Dependence as in Fig. 6 for the Extraction by 0.0302M Solution of TLA in Toluene

In the region of low concentrations of iron there are systematic positive deviations in the values of Z_A , particularly for the 2% and 5% solutions of TLA, while the agreement between the experimental and calculated values of Z_{Fe} is good in the whole measured range. Because in this range most of the citrates in the organic phase are bound in the form of binary amine-citric acid complexes and for the lowest Z_{Fe} the participation of complexes with iron on the total concentration of citrates in the organic phase is negligible, it can be assumed that these deviations are mainly due to the changes of the extraction properties of citric acid itself if turning to a system containing Fe.

In order to estimate the importance of individual complexes their content in some systems (0.0302M-TLA and 0.3075M-TLA) was calculated as a function of the equilibrium concentration of Fe in the aqueous phase, c_{Fe} .

From Figs 6 and 7 it follows that the most important complexes are actually those that can be derived by the substitution of FeA by H_3A in the complexes of H_3A with TLA, *i.e.*, the complexes (1,2,0), (1,4,2), and (3,6,2). The concentrations of complexes (2,4,0) and (2,5,1) are relatively low so that it can be assumed that these complexes do not represent real species but that they are rather factors given in the computational program terminology that express the deviations from the conditions required by the Guldberg-Waage law. The fact that the concentration of minor complexes increases with the increase of c_{Fe} , *i.e.*, with the increase of the non-ideality of the system, is in agreement with this assumption.

However, a different situation is with the complexes (1,4,4) and perhaps also (3,6,3) as they both participate substantially on the composition of solutions with both low and high values of c_{Fe} . The set of constants including the complex (1,4,4) (Table III) seems to describe better the data with low values of Z and at low pH values but the accuracy of these data, namely in these regions of Z and pH, is poorer which must be reflected in the much poorer agreement between the experimental and calculated results, particularly in the dependence $Z_A = f(c_{Fe,aq})$ as it was already discussed above. It seems therefore that along with the basic set of complexes (1,2,0), (1,4,2), and (3,6,2) there exists in the system at least one other complex in a comparable concentration. However, from the present data it cannot be unambiguously determined whether this complex is – relatively to Fe – a monomer (*e.g.*, (1,4,4)) or a polymer (*e.g.*, (3,6,3)).

Our results can be compared with the studies of Pyatnitskii and coworkers^{6,7} who found that in the extraction by solutions of various amines in toluene or chloroform the complex (1,4,2) is extracted from the citric acid solutions and the complex (1,4,4) from the malic acid solutions. This disagreement between the results obtained in this study and by Pyatnitskii and coworkers in the number of complexes is probably due to the fact that Pyatnitskii and coworkers derived the composition only from the slope of certain functions of the distribution ratio of Fe and, moreover, only for low values of $c_{Fe,aq}$ ($5 \cdot 10^{-4} \text{ mol l}^{-1}$). As pointed out, *e.g.*, by Danesi¹⁷ this method

does not give unambiguous results for the extraction systems with alkylamines. The simplifying assumptions that FeA is the predominant complex in the aqueous phase and that the amine forms with H_3A only one complex of the composition $(\text{TOA})_2\text{H}_3\text{A}$ are probably not fully correct. In the concentration range under study the complex FeA_2^{3+} participates significantly on the composition of the aqueous phase⁹. However, a more detailed study of the system $\text{TOA}-\text{H}_3\text{A}$ has not been done but in an analogous system $\text{TLA}-\text{H}_3\text{A}$ the complex $(\text{TLA})_3(\text{H}_3\text{A})_2$ exists⁸ in a concentration comparable with that of $(\text{TLA})_2(\text{H}_3\text{A})$.

So far the polymeric species were not found in the extractions from the organic acid solutions. Their existence is, however, understandable because the dimeric species $\text{Fe}_2\text{A}_2(\text{OH})_2^{2-}$ is the predominant component in the equilibrium aqueous phase at $c_{\text{Fe}} > 0.01 \text{ mol l}^{-1}$ (ref.⁹).

The composition of complexes as given in this paper is only formal, derived from the computational procedure and it does not express neither the structure of the extracted complex nor the nature of the bond. The formula $(1,4,2)$, i.e., $(\text{FeA})_4(\text{TLA})_4(\text{H}_3\text{A})_2$, means only that in the molecule the ratio Fe: TLA: (sum of citrate ions) is 1 : 4 : 3.

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