

EXTRACTION OF CITRIC ACID BY THE TOLUENE SOLUTIONS OF TRILAURYLAMINE

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The extraction of citric acid (H_3A) from the isomolar aqueous solutions of $1M-(Na, H)_3A$ and $(0.01-4)M$ solutions of pure citric acid by the toluene solutions of triaurylamine (TLA) has been studied. The complexes of the general composition of $(H_3A)_p(TLA)_q(H_2O)_r$, where $q = p + 1$, are extracted. The extraction isotherms in the system with $1M-(Na, H)_3A$ in the aqueous phase correspond best to the formation of complexes with the following values of (p, q) : (1, 2), (2, 3), and (5, 6). For the extraction systems with $(0.01-4)M H_3A$ in the aqueous phase the composition of the hydrated complexes can be expressed by the following values of (p, q, r) : the best set of complexes corresponds to (1, 2, 1), (2, 3, 2), and $(p, p + 1, p - 1 < r < p, \text{ where } p \text{ is } \sim 5)$, and also to one higher complex $(p, p, 0.65p, \text{ where } p > 10)$. The dissociation constants of citric acid in $1M-(H, Na)_3A$ have been determined, too.

Tertiary aliphatic amines (B) with long carbon chains are — due to their high basicity — good extraction agents for acids. However, the extraction equilibria and the composition of the ammonium salts produced depend substantially on the type of the acid (H_nA).

During the extraction of strong monobasic acids the anhydrous complexes of the composition $B_q(HA)_p$ are formed¹. The region of the formation of the neutral salt ($p = q$) extends usually into the region of high equilibrium concentrations of the acid in the aqueous phase. The deviations of the organic phase from the ideal behaviour are explained by the high association of ammonium salt molecules². Numerous similar extraction systems were thoroughly studied³.

On the other hand, organic monobasic acids form non-associated complexes of the type $B(HA)_p$, where p might be a rather high number (*e.g.* up to 4 in the case of acetic acid). The hydration degree is determined mainly by the value of p and reaches up to one water molecule per one acid molecule. From these types of systems the extractions of the acetic acid^{4,5}, trichloroacetic acid⁶, and nitro aromatic acids⁷ have been studied.

Dibasic acids, *e.g.* the sulphuric acid^{8,9}, form during the extraction in the first step the normal salt, *e.g.* $(B_2SO_4)_n$ which, during the subsequent extraction at higher aqueous acidities, is transformed into the hydrogen salt. Both the sulphate and the hydrogen sulphate are hydrated and both are associated, namely the hydrogen sul-

phate. Similar behaviour has been observed with organic dibasic acids but the existence of the normal salt (*e.g.* in the oxalic acid¹⁰) is somewhat dubious.

Pyatnitskii and coworkers¹¹ derived from the equilibrium data for the extraction of citric acid (H_3A) by trioctylamine that in the organic phase a complex with the citric acid: amine ratio 1 : 2 is formed, *i.e.* the ammonium salt has the total composition $B_2(H_3A)$.

In this paper the stoichiometry of the citric acid extraction by trilaurylamine has been studied over a rather wide concentration range. The results of this study are supposed to be applicable to the discussion of the extraction equilibria of metal ions in the system citric acid-TLA.

EXPERIMENTAL

Reagents

Trilaurylamine (Rhône-Poulenc) (TLA), citric acid (H_3A), sodium citrate (Na_3A), and toluene (all supplied by Lachema, analytical grade purity), were used without further purification.

The content of the tertiary amine in TLA was determined (after the acetylation of the primary and secondary amines by the acetanhydride according to Wagner and coworkers¹²) by the titration by the perchloric acid in acetic acid using the crystal violet as an indicator.

TLA solutions of the concentrations of 1, 2, 5, 10, and 20 vol.% were prepared by the precise weighing of TLA and by dilution by toluene to the given volume.

The citric acid content in stock solutions (2M and 4M) was determined by titration by the decarbonated sodium hydroxide using phenolphthalein as indicator. The sodium citrate content in the stock solution (1M) was determined by titration of a dried sample by the perchloric acid in acetic acid using the crystal violet as indicator¹³. The solutions used in the extraction experiments were prepared from these stock solutions by dilution.

Procedure

The samples were extracted by shaking identical volumes of initial solutions in extraction vessels at $25 \pm 0.25^\circ C$ in a thermostatted shaker. The time required for the thermal equilibrium establishment (2 hours) was found to be sufficient also for the establishment of the extraction equilibrium. After shaking the solutions were centrifugated. In the case that the organic phase was still turbid the solution was once more centrifuged after the separation of phases. Citric acid in the aqueous phase was titrated by the NaOH solution on phenolphthalein (similarly as in the stock solution), in the organic phase it was determined by the potentiometric two-phase titration by the decarbonated NaOH and in several cases also by titration by 0.1M sodium methoxide in pyridine using the azoviolet as an indicator.

In the series of measurements with $\geq 5\%$ TLA the content of water in the organic phase was determined by the Fischer method¹⁴. The amount of water extracted by pure toluene from solutions that did not contain sodium citrate was calculated using the known activity of water in the aqueous phase and the distribution constant of water for the extraction by toluene ($K_D = 0.026$) determined by Högfeldt¹⁵. The use of this constant is justified also by the fact that it was measured by the same method (*i.e.* by titration by the Karl Fischer reagent) as that used in this work. The dependence of the equilibrium concentration of water in toluene on the so-

dium citrate concentration in the aqueous phase (formed by the isomolar series of $1\text{M}-(\text{H}, \text{Na})_3\text{A}$) was determined experimentally (Fig. 1). The dissociation constants of citric acid in the system $1\text{M}-(\text{H}, \text{Na})_3\text{A}$ were determined from the potentiometric titration curve measured using the glass electrode (Metrohm EA-107 UX) and the silver chloride reference electrode connected with the measured solution by the bridge with 1M solution of Na_3A saturated with AgCl . Compensator E 388 (Metrohm, Switzerland) was used as the potentiometer. The pH scale was calibrated by the 1M solution of citric acid, the dissociation constants of citric acid necessary for the calculation of pH values being taken from the paper by Levien¹⁸ where they were determined by conductometry. The titration curves consist of two parts: the first one was obtained by the titration of $1\text{M}-\text{H}_3\text{A}$ by pure Na_3A solution and the second one by the inverse procedure, *i.e.* by the titration of $1\text{M}-\text{Na}_3\text{A}$ solution by $1\text{M}-\text{H}_3\text{A}$. Two curves were measured by each procedure, the agreement between them was better than 0.01 pH over the whole measured range.

RESULTS

The dissociation constants of citric acid were determined from the titration curve for the system $1\text{M}-(\text{H}, \text{Na})_3\text{A}$ plotted in the form of $\bar{n} = f(\log h)$, where $h = 10^{-\text{pH}}$, *i.e.* it means the concentration of hydrogen ions in the solution, $\bar{n} = (H - h) A_{\text{tot}}$, H = the analytical concentration of dissociable hydrogens in the solution, and $A_{\text{tot}} = 1$.

The results are presented in Table I and in Fig. 2 as average values from two measurements.

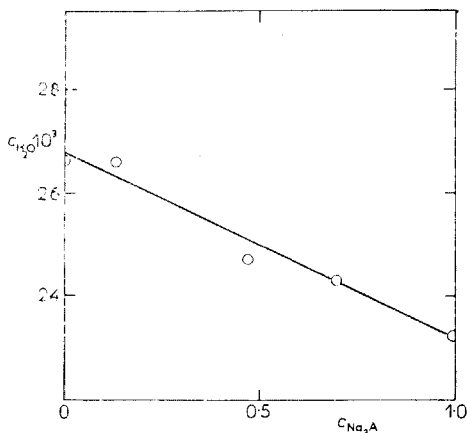


FIG. 1

The Dependence of the Extraction of Water by Toluene from $1\text{M}-(\text{H}, \text{Na})_3\text{A}$ on the Concentration of Na_3A in the Aqueous Phase Concentration expressed in mol l^{-1} .

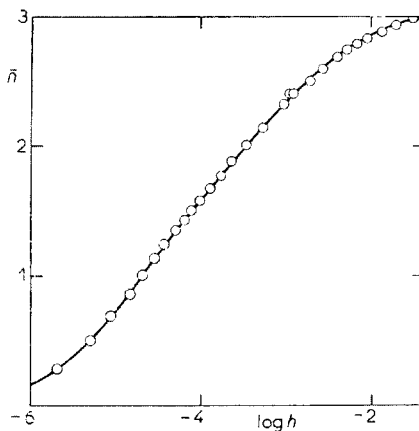


FIG. 2

The Titration Curve of Citric Acid in the $1\text{M}-(\text{H}, \text{Na})_3\text{A}$ System at 25°C

The full curve is calculated for $\log \beta_1 = 5.26$; $\log \beta_2 = 9.387$; $\log \beta_3 = 12.152$.

The extraction of citric acid was studied both in systems with a constant total concentration (1 mol/l) of citrates in the aqueous phase (Table II, Fig. 3), and in the citric acid solution of the concentration of 0.01–4 mol/l (Table III, Fig. 4). The experimental values are presented in the form of the function $Z = f(\log a)_B$. In the series with $\geq 5\%$ TLA, in which the extraction of water has also been measured, the values of $Z_{H_2O} = f(\log a)_B$ are also given, where B = the total concentration

TABLE I

Values of $\log h$ and \bar{n} Measured by the Titration of Citric Acid in the 1M-(H, Na)₃A System

–5.695, 0.274; –5.310, 0.500; –5.070, 0.693; –4.860, 0.859; –4.690, 1.002; –4.547, 1.127;
 –4.420, 1.237; –4.310, 1.335; –4.210, 1.423; –4.122, 1.499; –4.030, 1.578; –3.920, 1.666;
 –3.786, 1.764; –3.648, 1.874; –3.476, 1.999; –3.272, 2.141; –3.027, 2.305; –2.920, 2.378;
 –2.878, 2.398; –2.724, 2.497; –2.577, 2.583; –2.403, 2.673; –2.300, 2.721; –2.183, 2.770;
 –2.046, 2.820; –1.882, 2.872; –1.699, 2.992; –1.508, 2.969;

TABLE II

Equilibrium Values of $\log a$ and Z for the Citric Acid Extraction in the 1M-(H, Na)₃A-TLA-Toluene System

0.0155M-TLA

–1.153, 0.0249; –0.9162, 0.0427; –0.6954, 0.0631; –0.5194, 0.106; –0.3736, 0.145; –0.2474, 0.201; –0.1538, 0.241; –0.0747, 0.311; –0.0114, 0.334;

0.0305M-TLA

–1.407, 0.0258; –1.153, 0.0441; –0.902, 0.0847; –0.694, 0.136; –0.514, 0.188; –0.364, 0.260; –0.248, 0.323; –0.161, 0.387; –0.080, 0.440; –0.014, 0.467;

0.0771M-TLA^a

–2.255, 0.0104, –; –1.939, 0.0210, –; –1.647, 0.0357, 0.0765; –1.415, 0.0715, 0.0351; –1.172, 0.145, 0.140; –0.994, 0.160, 0.157; –0.826, 0.204, 0.170; –0.676, 0.272, 0.250; –0.514, 0.370, 0.362; –0.361, 0.459, 0.384; –0.256, 0.497, 0.499; –0.145, 0.551, 0.516; –0.071, 0.593, 0.522; –0.007, 0.618, 0.551;

0.306M-TLA^a

–2.915, 0.0056, –; –2.255, 0.0229, 0.0317; –1.859, 0.0696, 0.0715; –1.626, 0.126, 0.119; –1.353, 0.258, 0.327; –1.104, 0.408, 0.425; –0.888, 0.496, 0.510; –0.676, 0.593, 0.585; –0.514, 0.637, 0.617; –0.396, 0.676, 0.630; –0.265, 0.715, 0.670; –0.154, 0.740, 0.714; –0.075, 0.761, 0.698; –0.027, 0.768, 0.720;

^a The values of $\log a$, Z , and Z_{H_2O} are listed.

TABLE III

Equilibrium Values of $\log a_{\text{H}_3\text{A},\text{aq}}$, $\log a_{\text{H}_2\text{O},\text{aq}}$, $Z_{\text{H}_3\text{A}}$, and $Z_{\text{H}_2\text{O}}$ for 0.01–4M Citric Acid and for the Toluene Solution of TLA

0.03045M-TLA^a

−1.037, −0.001, 0.0604; −0.719, −0.002, 0.121; −0.538, −0.002, 0.181; −0.283, −0.004, 0.286;
−0.082, −0.007, 0.393; 0.083, −0.010, 0.467; 0.536, −0.024, 0.673; 1.119, −0.068, 0.867; 1.528,
−0.113, 0.965;

0.07715M-TLA

−1.064, −0.001, 0.119, 0.113; −0.872, −0.001, 0.174, 0.224; −0.745, −0.002, 0.222, 0.224;
−0.636, −0.002, 0.277, 0.286; −0.410, −0.003, 0.386, 0.327; −0.302, −0.004, 0.450, 0.360;
−0.062, −0.007, 0.546, 0.469; 0.067, −0.009, 0.604, 0.489; 0.098, −0.010, 0.618, 0.551; 0.323,
−0.016, 0.688, 0.548; 0.531, −0.024, 0.757, 0.592; 0.708, −0.033, 0.803, 0.608; 0.939, −0.053,
0.854, 0.619; 1.130, −0.069, 0.901, 0.613; 1.411, −0.104, 0.976, 0.585; 1.466, −0.113, 0.979, 0.572;

0.1520M-TLA

−1.606, 0.000, 0.0689, 0.0659; −1.208, −0.001, 0.193, 0.176; −0.860, −0.001, 0.352, 0.356;
−0.640, −0.002, 0.448, 0.433; −0.364, −0.004, 0.556, 0.534; −0.136, −0.006, 0.639, 0.614;
0.092, −0.010, 0.706, 0.629; 0.502, −0.023, 0.808, 0.673; 0.610, −0.028, 0.835, 0.688; 1.078,
−0.063, 0.936, 0.661; 1.496, −0.115, 1.006, 0.651;

0.3062M-TLA

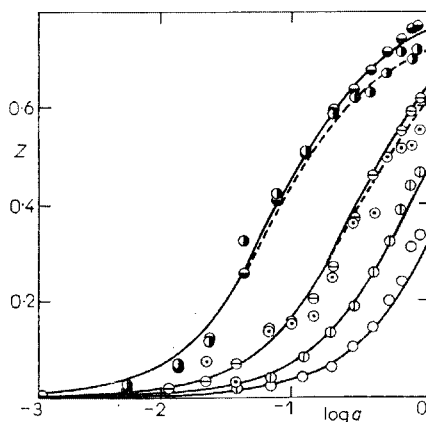
−2.131, 0.00, 0.0335, 0.0490; −1.733, 0.00, 0.0952, 0.121; −1.456, 0.00, 0.205, 0.235; −1.289,
0.000, 0.311, 0.353; −1.136, −0.001, 0.407, 0.435; −0.986, −0.001, 0.473, 0.500; −0.883, −0.001,
0.537, 0.549; −0.506, −0.003, 0.641, 0.618; −0.036, −0.007, 0.754, 0.664; 0.112, −0.010, 0.755,
0.714; 0.241, −0.013, 0.798, 0.688; 0.458, −0.021, 0.833, 0.709; 0.647, −0.030, 0.881, 0.701;
0.856, −0.044, 0.917, 0.694; 1.072, −0.062, 0.959, 0.687; 1.343, −0.095, 0.993, 0.676;

^a The value $Z_{\text{H}_2\text{O}}$ was not determined for the system with 0.03045M-TLA.

FIG. 3

The Extraction of Citric Acid and Water by the Solution of TLA in Toluene from 1M-(H, Na)₃A

The dependence of Z (○, ⊕, ⊖, ⊙) and $Z_{\text{H}_2\text{O}}$ (⊙, ⊕) on $\log a_{\text{H}_3\text{A}}$ ($= \log [\text{H}_3\text{A}]_{\text{aq}}$). The organic phase: 0.0155M-TLA — ○; 0.0305M-TLA — ⊕; 0.0771M-TLA — ⊖, ⊙ and 0.306M-TLA — ⊙, ⊕. The full curves were calculated for $\log \beta_{1,2} = 1.35$, $\log \beta_{2,3} = 3.06$, and $\log \beta_{5,6} = 8.94$, the dashed curve ($Z_{\text{H}_2\text{O}}$) for $\frac{[(\text{H}_3\text{A})_5(\text{TLA})_6(\text{H}_2\text{O})_4]}{[(\text{H}_3\text{A})_5(\text{TLA})_6(\text{H}_2\text{O})_5]} = 0.426$. The bar over the formula means the organic phase.



of the amine in the organic phase, a = the citric acid activity in the aqueous phase (in the systems with $1M-(H, Na)_3A$ in the aqueous phase the value of a was taken to be equal to $[H_3A]$), Z = (the total concentration of citrates in the organic phase)/ B , Z_{H_2O} = (the concentration of water in the organic phase – the concentration of water extracted by toluene)/ B .

The activities of citric acid and water in aqueous solutions at 25°C. The activities of non-dissociated citric acid (*i.e.*, of the H_3A species) in the aqueous phase are taken from the paper by Levien¹⁶ in which the values of activities and densities of the H_3A solutions of ≤ 1 mol/l were published. However, the experimental isopiestic data in this paper¹⁶ cover the entire concentration range up to the saturation (≈ 4.3 mol/l). In the calculation of the osmotic and activity coefficients from the isopiestic data Levien¹⁶ took also into the consideration the effect of ions formed by the dissociation of citric acid using the values of the dissociation degree, $\alpha = [H_2A^-]/c = [H^+]/c$, determined from the measurements of conductivity, where c is the total concentration of citric acid. The results of the conductivity measurements are given also only for solutions in which the concentration of citric acid $\leq 1M$.

The citric acid activities in solutions $> 1M-H_3A$ were calculated from the experimental data of Levien¹⁶ assuming on the base of the citric acid activity values at $\leq 1M-H_3A$ that: a) the first dissociation constant does not change in the region

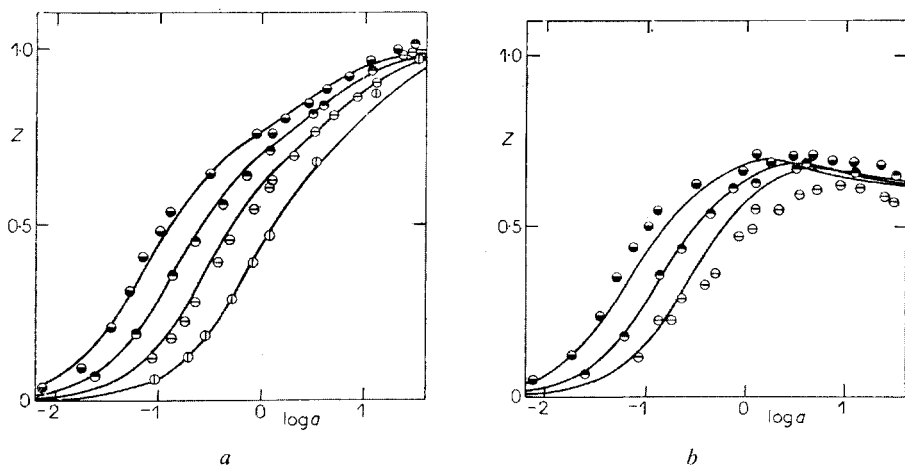


FIG. 4

The Extraction of Citric Acid and Water by the Solution of TLA in Toluene from 0.01–4M Solutions of Citric Acid in Water

The dependence of Z_{H_3A} (4a) and Z_{H_2O} (4b) on $\log a_{H_3A}$ in the aqueous phase is plotted. \odot 2% TLA; \square 5% TLA; \bullet 10% TLA; \blacksquare 20% TLA; The full curves are calculated for $\log \beta_{1,2,1} = 1.17$; $\log \beta_{2,3,2} = 3.17$; $\log \beta_{5,6,4} = 8.39$; $\log \beta_{5,6,5} = 8.49$ and $\log \beta_{13,13,8} = 19.14$.

1 – 4.3M-H₃A and the dissociation to the second step is negligible, and *b*) the dissociation degree in this region is approximately given by the relation $\alpha = \text{const. } c^{-1/2}$. The highest value of α in this region is 0.03 in 1M-H₃A so that the error introduced by these two assumptions is small if compared with the accuracy of the experimental extraction data to the interpretation of which the activities are used.

The values of activity coefficients have been recalculated from the molality to the molarity scale using the experimentally determined densities of citric acid (Table IV) and also several other data from the published literature^{16,17}. Table V presents the calculated values of the activity coefficients of the non-dissociated citric acid.

The activity of water in the citric acid solutions (Table VI) was determined from the activities of water in corresponding isopiestic solutions using the data of Levien¹⁶ on the composition of the corresponding NaCl solutions and those of Robinson and Stokes¹⁸ on the activity of water in NaCl solutions.

TABLE IV
The Dependence of the Citric Acid Solution Densities at 25°C on the Concentration

<i>c</i> , mol/l	ρ , g/cm ³	<i>c</i> , mol/l	ρ , g/cm ³
0.5046	1.0362	2.487	1.1837
1.014	1.0744	2.977	1.2196
1.261	1.0931	3.413	1.2493
1.521	1.1122	3.650	1.2665
1.745	1.1287	4.259	1.3058
2.015	1.1498		

TABLE V
Activity Coefficients of the Non-Dissociated Citric Acid (γ_c) in the Aqueous Solutions at 25°C^a

<i>c</i> _{H₃A} , mol/l	γ_c	<i>c</i> _{H₃A} , mol/l	γ_c	<i>c</i> _{H₃A} , mol/l	γ_c
0.974	1.233	2.714	2.466	3.661	4.404
1.274	1.353	2.935	2.787	3.815	4.918
1.618	1.517	3.136	3.143	3.958	5.446
1.931	1.711	3.323	3.540	4.092	6.010
2.215	1.931	3.498	3.953	4.210	6.647
2.475	2.182				

^a Calculated from the data of Levien¹⁶.

Dissociation of citric acid in the $1M-(H, Na)_3A$ system. The values of the total protonization constants of citric acid were calculated by a graphical method according to Leden and Fronaeus¹⁹ from the experimental data for $\bar{n} = f(\log h)$ (cf. Table I) assuming that the activity coefficients of hydrogen ions and of the citric acid anions are constant.

The values of the constants were refined using the computer program LETAGROPVRID written by Sillén and Ingri²⁰.

TABLE VI
Activity of Water in the Citric Acid Solutions at 25°C^a

c_{H_3A} , mol/l	a_{H_2O}	c_{H_3A} , mol/l	a_{H_2O}	c_{H_3A} , mol/l	a_{H_2O}
0.2037	0.99596	1.413	0.96645	3.423	0.8590
0.2035	0.99596	1.450	0.96524	3.498	0.8534
0.2045	0.99592	1.845	0.9517	3.729	0.8319
0.2960	0.99413	2.020	0.9447	3.802	0.8251
0.3736	0.99256	2.031	0.9445	3.990	0.8052
0.5062	0.98975	2.060	0.9432	4.105	0.7926
0.5094	0.98972	2.298	0.9325	4.153	0.7867
0.6014	0.98770	2.648	0.9143	4.210	0.7794
0.7134	0.98520	2.929	0.8970	4.228	0.7771
0.7922	0.98337	3.198	0.8776		
0.9316	0.97996	3.295	0.8701		
1.0718	0.97636	3.334	0.8668		

^a Calculated from the isopiestic data of Levien¹⁶ for the $H_3A-NaCl$ pair and from the data of Robinson and Stokes¹⁸ for the activity of water in NaCl.

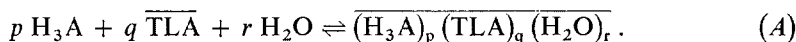
TABLE VII
Protonization Constants of Citric Acid at 25°C

Medium	$\log K_1$	$\log K_2$	$\log K_3$	Ref.
2M- $NaClO_4$	5.18 ± 0.03	4.16 ± 0.05	2.90 ± 0.07	(22)
3M-($NaClO_4$)	4.88	3.83	2.40	(23)
0.1M- KNO_3	5.65	4.30	2.79	(24)
1M- KNO_3	5.34	4.11	2.63	(24)
2M- KNO_3	5.49	4.39	3.08	(21)
1M-(H, Na) ₃ A	5.25 ₅	4.14	2.76	this work (graphical method)
1M-(H, Na) ₃ A	5.23 ± 0.03	4.16 ± 0.03	2.76 ± 0.03	this work (LETAGROPVRID)

From Table VII it is evident that these constants agree quite well with those measured at higher concentrations of background electrolytes and that the assumption on the constancy of the activity coefficients of individual components in 1M-(H, Na)₃A can be taken as justified. Migal and Sychev²¹, in contrast to Bottari and Vicedomini²², assume also the dissociation of the alcoholic group. The eventual existence of the H₋₁A species relates only to the region outside the scope of our measurements and therefore it has not been considered in our computations.

The treatment of the experimental data on the citric acid extraction. The interpretation of the citric acid extraction by a tertiary amine in a non-polar solvent is based on the generally accepted assumption that the extracted components are the electroneutral ion pairs.

The citric acid extraction can therefore be described *e.g.*, by a set of equations of the type



Using this notation the dissociation constants of citric acid need not be known, only the activities of the H₃A species.

Assuming that the activity coefficients of all components in the organic phase are unity, the equilibrium constant for equation (A) is given by the expression

$$\beta_{p,q,r} = \frac{[\overline{(\text{H}_3\text{A})_p (\text{TLA})_q (\text{H}_2\text{O})_r}]}{[\text{H}_3\text{A}]^p [\overline{\text{TLA}}]^q \{\text{H}_2\text{O}\}^r}. \quad (1)$$

The values in brackets are the stoichiometric concentrations, those in braces are the activities. The concentrations of the species in the organic phase are denoted by bars; $\{\text{H}_2\text{O}\}$ might be considered constant (within $\pm 3\%$) in the whole series of 1M-(H, Na)₃A and in the series (0.01–4)M-H₃A for $c_{\text{H}_3\text{A}} \leq 1\text{M}$.

In the first step the type of the extracted complexes has been derived, then their composition has been determined and the values of extraction constants have been calculated by a graphical method and finally these values were refined by a computer calculation^{23,24}. The possibility to interpret the experimental data by a larger set of complexes, that cannot be treated by a graphical method, has been tested also by a computer calculation.

The type of extracted complexes was determined from the form of the function $\bar{q} = f(\bar{p})$, where \bar{q} and \bar{p} are the average values of the indexes p and q of the complex (*cf.* equation (A)). The method, worked out by Sillén²⁵ and adapted in the form of the computer program MESAK²⁶, has been used for the evaluation of \bar{p} and \bar{q} . According to this method the auxiliary functions

$$R = \text{const.} + \int (\partial \log a / \partial \log B)_Z dZ \quad (B = \text{const.}) \quad (2)$$

and

$$\ln \alpha_0 = \ln b - \ln B = \text{const.} - \int [Z + (\partial Z / \partial \ln B)_a] d \ln a (B = \text{const.}) \quad (3)$$

are computed in the first step and then

$$\bar{p} = Z / (R - \alpha_0)$$

and

$$\bar{q} = (1 - \alpha_0) / (R - \alpha_0). \quad (4)$$

The concentration of free amine in the organic phase (b) is computed simultaneously by the Eq. (3).

The dependence of \bar{q} on \bar{p} , *i.e.* the average composition of the complexes in the individual experimental points, is presented in Figs 5 and 6 for both systems under study. The lowest complex corresponds to the formula $(\text{TLA})_2(\text{H}_3\text{A})$ followed by a series of complexes of the type $(\text{TLA})_q(\text{H}_3\text{A})_p$ with $q = p + 1$.

The equilibrium constants (l) of extracted complexes were calculated from the equation

$$BZ = \beta_{1,2}ab^2 + 2\beta_{2,3}a^2b^3 + 3\beta_{3,4}a^3b^4 + \dots, \quad (5)$$

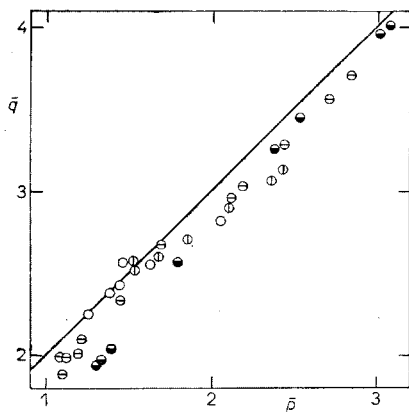


FIG. 5

The Dependence of \bar{q} on \bar{p} for 1M-(H, Na)₃A-TLA-Toluene

○ 1% TLA; ⊙ 2% TLA; ⊕ 5% TLA;
● 20% TLA.

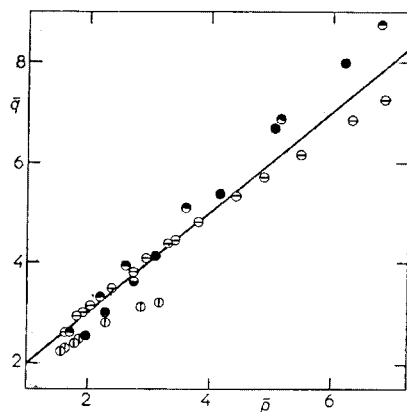


FIG. 6

The Dependence of \bar{q} on \bar{p} for 0.01-4M H₃A-TLA-Toluene

⊙ 2% TLA; ⊕ 5% TLA; ⊔ 10% TLA; ● 20% TLA.

which can be rewritten in the form ($u = ab$)

$$BZ/ab^2 = \beta_{1,2} + 2\beta_{2,3}u + 3\beta_{3,4}u^2 + \dots, \quad (6)$$

where B , Z , and a are the experimental values and b can be obtained by the program MESAK. The computation has been performed graphically by fitting a normalized curve to the experimental function.

The system 1M-(H, Na)₃A-TLA-toluene. The dependence of $\log BZ/ab^2$ on $\log u$ is given in Fig. 7. The shape of this curve demonstrates that the complex (1, 2) predominates at low values of u while higher complexes are formed with the increase of u . The horizontal asymptote to this curve gives $\log \beta_{1,2}$ on the y-axis and the vertical asymptote determines $\log K'_s$ on the x-axis (cf. below). For $u \leq 0.007$ the value of BZ/ab^2 depends linearly on u (Fig. 8). This line has a slope of $2\beta_{2,3}$ and the corresponding ordinate on the y-axis is $\beta_{1,2}$. From this graph the value of $\log \beta_{1,2} = 1.32 \pm 0.25$ has been determined. The error corresponds to the two limiting positions of the normalized curves (cf. the dotted lines) that still fit the experimental points.

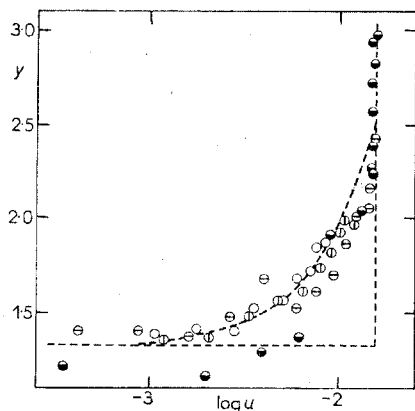


FIG. 7

The Dependence of $y = \log(BZ/ab^2)$ on $\log u$ for 1M-(H, Na)₃A-Toluene

○ 1% TLA; ○● 2% TLA; ○⊗ 5% TLA; ● 20% TLA. The values of asymptotes correspond to the values of $\log \beta_{1,2} = 1.32$ and $\log K'_s = -1.81$ (cf. Eq. (2)). The dashed curve is calculated for $\log \beta_{1,2} = 1.26$; $\log \beta_{2,3} = 3.22$, and $\log \beta_{5,6} = 8.95$.

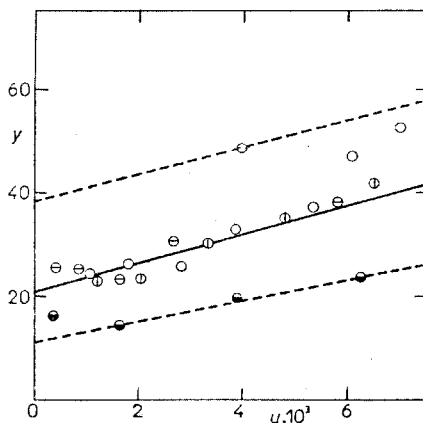


FIG. 8

The Dependence of $y = BZ/ab^2$ on u for 1M-(H, Na)₃A

○ 1% TLA; ○● 2% TLA; ○⊗ 5% TLA; ● 20% TLA. The full curve corresponds to the values of $\beta_{1,2} = 20.9$ ($\log \beta_{1,2} = 1.32$) and $\beta_{2,3} = 1320$, the dashed curve to $\log \beta_{1,2} = 1.32 \pm 0.25$.

The composition of the subsequent complex has been determined by fitting the dependence $\log y = \log ((BZ/ab^2 - \beta_{1,2})/u)$ on $\log u$ to a series of normalized curves of the type $\log(1 + x^i)$ vs $\log x$ for $i = 1, 2, 3$. If we assume that along with the (1, 2) and (2, 3) complexes there exists (within certain limits of u) still one other complex of the type $q = p + 1$, then the expression suitable for the graphical computation can be obtained by rearranging Eq. (6) into the form

$$y = (BZ/ab^2 - \beta_{1,2})/u = 2\beta_{2,3} + (i + 2)\beta_{i+2,i+3} \cdot u^i. \quad (7)$$

Substituting

$$v = ((i + 2)\beta_{i+2,i+3})/2\beta_{2,3} \quad \text{and} \quad x = v^{1/i}u \quad (8)$$

we finally get

$$y = 2\beta_{2,3}(1 + x^i). \quad (9)$$

The last equation was used in the logarithmic form

$$\log y = \log(2\beta_{2,3}) + \log(1 + x^i). \quad (10)$$

The value of $\log(2\beta_{2,3})$ is given by the vertical shift of the normalized curve $\log(1 + x^i)$ vs $\log x$ with respect to the experimental curve $\log y$ vs $\log u$. For the value of $\log \beta_{i+2,i+3}$ we have

$$\log \beta_{i+2,i+3} = i(\Delta \log x) + \log \beta_{2,3} + \log 2 - \log(i + 2), \quad (11)$$

where $\Delta \log x = \log x - \log u$ represents the horizontal shift of both functions.

Fig. 9 presents the graphical calculation for the (2, 3) and (5, 6) complexes. The full curve in the graph corresponds to the calculated constants. The error of the evaluation of constants was again determined from the limiting positions of the normalized curves (the dash-and-dot curves). The graphical fitting of the experimental function to the normalized curve for the (2, 3), (5, 6) system is better than for the other systems, *e.g.* (2, 3), (4, 5).

The value of $\log \beta_{2,3}$, obtained from the horizontal shift of the normalized curve, is 3.14 ± 0.24 . The corresponding value of $\log \beta_{5,6}$ is $8.77_{+0.32}^{-0.13}$.

It follows from Figs 5 and 6 that p and q attain relatively high values. The values of \bar{p} , \bar{q} for 20% TLA are not presented for the whole concentration range studied because two points with the same value of Z for various B 's are requested as minimum for the computation of the derivative in Eqs (2)–(4).

However, the composition of higher complexes cannot be determined due to the high scatter of experimental values in this region. Therefore, as an alternative, the

Högfeldt's treatment²⁷ has been used, according to which all higher complexes are expressed as one symbolic complex with $p \approx q \rightarrow \infty$, the equilibrium constant of which is given by

$$K'_S = \frac{[(\text{TLA} \cdot \text{H}_3\text{A})_{\text{aggr}}]}{\{\text{H}_3\text{A}\} [\text{TLA}]} \quad (12)$$

The value of this constant, together with the value of $\beta_{1,2}$, was determined from the asymptotes to the curve in Fig. 7.

The individual models were then compared from the aspect of their statistical probability and the values of equilibrium constants were determined more precisely using the computational program LETAGROP²⁸⁻³⁰. By this program the minimum of the function

$$U = \sum (f(\Delta Z))^2 \quad (13)$$

is sought using the variation of the values of $\beta_{p,q,r}$. The difference ΔZ between the experimental value of $Z(Z_{\text{exp}})$ and the value of Z calculated for the given set of $\beta_{p,q,r}$ was accepted as the function $f(\Delta Z)$. The weight of individual points was assumed to be proportional to $(Z_{\text{exp}})^{1/2}$.

This type of weighing was chosen as a compromise between the use of the absolute error $f(\Delta Z) = \Delta Z$, when the effect of points with the lowest value of Z is practically neglected, and the use of the relative error $f(\Delta Z) = \Delta Z/Z$, when a too high weight is ascribed to points with relatively lower precision, *i.e.* to points with a low value of Z .

The comparison of the individual models is given in Table VIII. The values of β , U , and the standard deviation σ are quoted for the individual models. The errors of constants have been calculated from the standard deviation of the constant k (henceforth denoted $s(k)$) as $\pm 3s(k)$. If $k < 5s(k)$, only the maximum value of k , equal to $k + 3s(k)$, is given. From this table it is evident that from all models with 3 complexes the combination of (1, 2), (2, 3), and (5, 6) complexes yields the lowest value of $U = 2.97 \cdot 10^{-2}$. However, the complex (5, 6) must be considered only as a representative of higher complexes because, *e.g.*, the (6, 7) complex yields nearly the same value of $U = 3.01 \cdot 10^{-2}$.

Combinations of four complexes have been taken into the consideration, too, but it has been found that any substitution of the (5, 6) complex by two other complexes does not substantially decrease the value of U . The best combination of 4 complexes, *i.e.* (1, 2), (2, 3), (3, 4), and (6, 7), gives $U = 2.877 \cdot 10^{-2}$.

The computational treatment of 5-complex models reduces finally to a model with 4 complexes as the minimum of the function (15) was found for one equilibrium constant equal to zero.

On the other hand, the interpretation of the experimental data with the combination of the (1, 2) complex with a single other complex, *e.g.* (4, 5) or (5, 6), is evidently not realistic as the values of U for these models are $3.541 \cdot 10^{-2}$ and $4.224 \cdot 10^{-2}$, respectively.

The agreement between the theoretical isotherm and the experimental points can be substantially improved assuming that a certain part of the extracted acid exists in the form of (p, p)-type complexes. The program LETAGROP presents the average value of $p \approx 3$. The corresponding value of $U = 0.0166$ and the systematic deviation for $\log a \rightarrow 0$ for 1 and 2% TLA is suppressed (Fig. 3). However, it is impossible to decide whether this deviation is really caused by the presence of (3, 3) complexes or by the change of the activity coefficients in the organic phase at various concentrations of the citrate amine.

System (0.01–4)_M-H₃A–TLA–toluene. The extraction from (0.01–4)_M-H₃A is interpreted similarly as the extraction from 1_M-(H, Na)₃A. Fig. 10 presents the de-

TABLE VIII

Comparison of the Models for the Interpretation of the Citric Acid Extraction from 1_M-(H, Na)₃A by the Toluene Solution of TLA

Model	Logarithms of the constants	U	σ
(1, 2), (2, 3), (5, 6), (∞, ∞),	1.32 ± 0.25 ; 3.14 ± 0.24 ; 8.77 ± 0.32 ; $\log K'_s = -1.81$	graphical	method
(1, 2), (2, 3), (5, 6),	1.26 ± 0.25 ; 3.22 , max 3.43 ; 8.95 ± 0.20	0.02971	0.02598
(1, 2), (2, 3), (4, 5),	1.41 ± 0.11 ; 1.83 , max 3.31 ; 7.28 ± 0.11	0.03538	0.02804
(1, 2), (2, 3), (6, 7),	1.14 , max 1.37 ; 3.39 ± 0.16 ; 10.66 ± 0.22	0.03010	0.02615
(1, 2), (2, 3), (3, 4), (6, 7),	1.30 , max 1.57 ; 2.91 , max 3.65 ; 5.08 , max 5.58 ; 10.56 , max 10.81	0.02877	0.02587
(1, 2), (2, 3), (4, 5), (6, 7),	1.25 , max 1.49 ; 3.21 , max 3.56 ; 6.78 , max 7.29 ; 10.50 , max 10.83	0.02896	0.02595
(1, 2), (2, 3), (5, 6), (6, 7)	1.22 , max 1.46 ; 3.29 , max 3.54 ; 8.71 , max 9.27 ; 10.28 , max 10.95	0.02922	0.02607
(1, 2), (2, 3), (3, 4), (5, 6),	reduces to (1.2), (2.3), (5.6)		
(1, 2), (2, 3), (5, 6), (3, 3),	1.30 ± 0.23 ; 3.05 ± 0.16 ; 8.66 ± 0.21 3.05 ± 0.19 ;	0.01656	0.01924
(1, 2), (4, 5),	1.42 ± 0.10 ; 7.28 ± 0.10	0.03541	0.02805
(1, 2), (5, 6),	1.51 ± 0.09 ; 9.15 ± 0.14	0.04224	0.03063

FIG. 9

The Dependence of $y = \log((BZ/ab^2 - \beta_{1,2})/u)$ on $\log u$ for 1M-(H, Na)₃A and $Z < 0.62$

○ 1% TLA; ⊙ 2% TLA; ⊕ 5% TLA; ● 20% TLA. The full curve is calculated for the values of constants $\log \beta_{2,3} = 3.14 \pm 0.24$ and $\log \beta_{5,6} = 8.77^{+0.32}_{-0.13}$. The precision of constants is indicated by dashed curves.

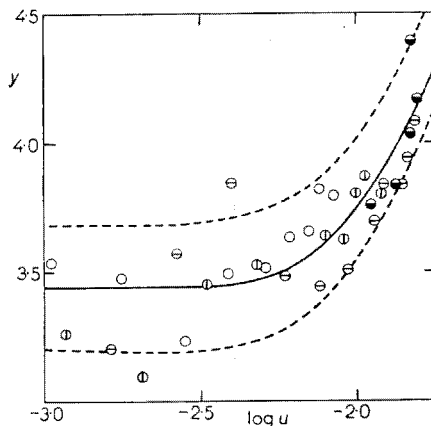


FIG. 10

The Dependence of $y = \log(BZ/ab^2)$ on $\log u$ for 0.01–1.5M-H₃A

○ 2% TLA; ⊕ 5% TLA; ● 10% TLA; ● 20% TLA. The asymptotes correspond to the values of $\log \beta_{1,2} = 1.25$ and $\log K'_5 = -1.70$. The dashed curve is calculated for $\log \beta_{1,2} = 1.17$; $\log \beta_{2,3} = 3.17$; $\log \beta_{5,6} = 8.74$.

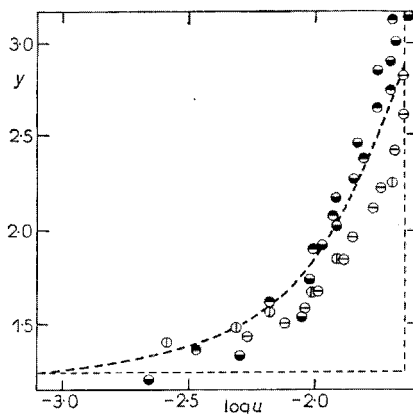
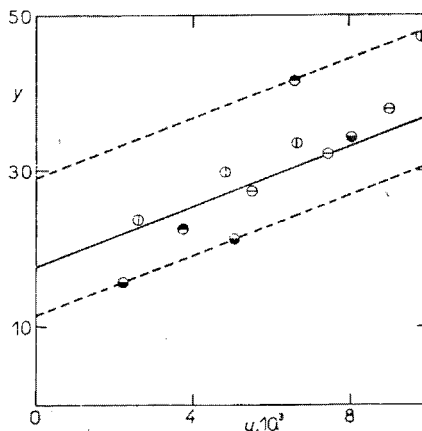


FIG. 11

The Dependence of $y = (BZ/ab^2)$ on u for $u < 0.009$ in 0.01–4M-H₃A

○ 2% TLA; ⊕ 5% TLA; ● 10% TLA; ● 20% TLA. The straight lines on the graph correspond to $\log \beta_{1,2} = 1.25 \pm 0.18$, $\log \beta_{2,3} = 2.84$. The precision of the constant $\beta_{1,2}$ is indicated by dashed straight lines.



pendence of $\log BZ/ab^2$ on $\log u$. The asymptotes to the curve correspond to the constants $\log \beta_{1,2} = 1.25$ and $\log K'_s = -1.7$. It is evident from Fig. 11 that the (1, 2) complex changes into (2, 3) similarly as in the previous system. The corresponding value of $\log \beta_{1,2}$ is 1.25 ± 0.18 . The values of the constants $\log \beta_{2,3} = 2.84 \pm 0.16$ and $\log \beta_{5,6} = 8.82 \pm 0.32$ have been determined by the method of the normalized curve (Fig. 12). The data treatment by the program LETAGROP takes into account also the coextraction of water and it is explained by the assumption of the formation of hydrated complexes.

Coextraction of Water. Because the amount of extracted water increases with the increasing extraction of H_3A , it can be assumed that the complexes of citric acid with the amine are hydrated. The composition of hydrated complexes has been determined using the results obtained for the extraction of citric acid by 5–20% amine (Table III).

For the solutions of pure citric acid of the concentration 0.2 mol/l and for the H_3A concentration ≤ 0.7 mol/l in the system 1M-(H, Na)₃A ($a \leq 0.18$) it can be assumed that approximately $Z_{H_2O} = Z$ (cf. Tables II and III) so that the composition of the lowest two complexes is $(H_3A)(TLA)_2H_2O$ and $(H_3A)_2(TLA)_3(H_2O)_2$.

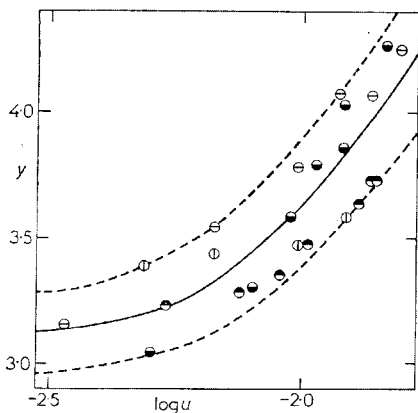


FIG. 12

The Dependence of $y = \log \left(\frac{BZ/ab^2 - \beta_{1,2}}{ab} \right)$ on $\log u$ for 0.01–4M- H_3A and for $\log u < -1.8$

○ 2% TLA; □ 5% TLA; ● 10% TLA; ◐ 20% TLA. The curves in the figure correspond to $\log \beta_{2,3} = 2.84 \pm 0.16$ and $\log \beta_{5,6} = 8.82 \pm 0.32$.

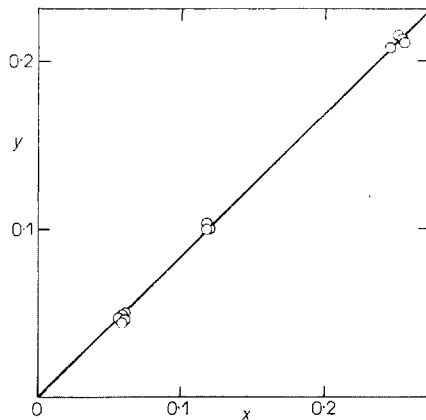


FIG. 13

The Determination of the Distribution Constant K_D for the Distribution of Water between the Aqueous Phase and the $(TLA H_3A)_{agg}$ Phase for $Z \geq 0.835$

The dependence of $y = c_{H_2O,org}$ on $x = c_{H_3A,org} \cdot a_{H_2O,aq}$.

In the region of the highest equilibrium concentrations of H_3A in the aqueous phase $Z_{H_2O} < Z$. In this region H_3A is present in the organic phase in the form of highly polymerized complexes, *i.e.* in the form of the aggregate phase $(TLA H_3A)_{aggr}$. The extraction of water can be described as its distribution between the aqueous phase and the $(TLA H_3A)_{aggr}$ phase. This assumption is evidently valid for $Z \geq 0.835$ because in this region the corresponding equilibrium constant K_D has a constant value (Fig. 13):

$$K_D = [H_2O]_{org}/a_{H_2O,aq}[TLA H_3A]_{aggr} \approx [H_2O]_{org}/a_{H_2O,aq} \cdot [H_3A]_{org} = 0.843. \quad (14)$$

The average number of water molecules contained in the (5, 6) complex can be determined (neglecting the higher complexes, *i.e.* for the H_3A concentrations < 1.5 mol/l in the aqueous phase) from Eq. (15) derived from the mass balance of H_3A and H_2O in the organic phase:

$$\bar{r} = 5((BZ_{H_2O}/ab^2) - \beta_{1,2} - \beta_{2,3u})/((BZ/ab^2) - \beta_{1,2} - \beta_{2,3u}). \quad (15)$$

The average value $\bar{r} = 4.36$ has been obtained (the program LETAGROP yields $\bar{r} = 4.43$ for 1M-(H, Na) $_3$ A).

The composition of the organic phase can therefore be formally described by a set of complexes of the type $(TLA)_p(H_3A)_q(H_2O)_r$ where the indexes (p, q, r) are (1, 2, 1), (2, 3, 2), (5, 6, 5), and (5, 6, 4), respectively. However, as the complex (5, 6) was assumed to be more a representative of higher complexes rather than the only real species in this size range, the system of hydrated complexes can be better described as (1, 2, 1), (2, 3, 2), and $(p, p + 1, (p - 1) < r < p)$, where p is ~ 5 . The final treatment has been done by the computer program LETAGROP. The minimum of the weighted sum of relative errors has been sought, *i.e.* the minimum of the expression

$$f(\Delta Z) = ((Z_{calc} - Z_{exp})/Z_{calc})_{H_3A} + w((Z_{calc} - Z_{exp})/Z_{calc})_{H_2O}, \quad (16)$$

where w is the weight, the value of which has been chosen to be 0.5 to express the lower precision of the determination of water in comparison with the acid determination precision. These calculations have been done over the whole concentration range. High polymers existing at the aqueous citric acid concentrations $> 1.5M$ have been included into one symbolic complex $(H_3A)_p(TLA)_q(H_2O)_{yp}$.

The average values of p and y have been calculated by the program LETAGROP assuming two models ($q = p + 1$ and $q = p$) together with the corresponding values of the equilibrium constants of (1, 2, 1), (2, 3, 2), (5, 6, 4), (5, 6, 5), and (p, q, yp) complexes. In the first case $q = p + 1 = 90$ has been obtained while in the second one we have got $q = p \approx 13$. The value of y is in both cases ≈ 0.65

which agrees with the ratio $Z_{\text{H}_2\text{O}}/Z_{\text{H}_3\text{A}}$ in the given concentration range. Because the agreement for the model $q = p$ is somewhat better than that for the model $q = p + 1$ ($U = 0.610$ and 0.648 , respectively), the most probable stoichiometric composition of the remaining complex is (13, 13, 8). The corresponding values of the equilibrium constants are as follows: $\log \beta_{1,2,1} = 1.17 \pm 0.22$, $\log \beta_{2,3,2} = 3.17$, max. 3.38 , $\log \beta_{5,6,4} = 8.39 \pm 0.05$, $\log \beta_{5,6,5} = 8.49$, max. 8.77 , and $\log \beta_{13,13,8} = 19.14 \pm 0.013$.

The curves $Z_{\text{H}_3\text{A}} = f(\log a_{\text{H}_3\text{A}})$ and $Z_{\text{H}_2\text{O}} = f(\log a_{\text{H}_3\text{A}})$ calculated for this set of complexes are presented in Fig. 4.

It is evident that the acid extraction is well described by the given model while for the extraction of water there are deviations from the experimental values, namely at 5 and 20% of TLA. However, we cannot be sure whether these differences are caused by the presence of other complexes or, *e.g.*, by the change of water solubility in the solvent, by the changes of the activity coefficients due to the increase of the organic phase polarity, *etc.*, so that any attempt to try other, more complex models seems pointless. Generally it can be concluded that the (1, 2, 1) and (2, 3, 2) complexes are transformed into higher complexes of the $(p, p + 1, p - x)$ type, where $0 < x < 1$. At the acid concentration in the aqueous phase $> 1\text{M}$ a mixture of $(p, p + x, yp)$ complexes is formed, where $0 \leq x \leq 1$, and y is ~ 0.65 .

DISCUSSION

The extraction of citric acid by trilaurylamine has been studied in the course of a wider program of the studies of metal ion extraction by amines from the solutions of citrates. As the mineral acids form stronger complexes with amines than the citric acid, extraction systems containing no mineral acids had to be chosen otherwise the mineral acid would be extracted preferentially and the equilibria under study would be more complicated.

However, this made the control of the activity coefficients of the solution components more difficult as this is usually done by using a constant ionic medium maintained by an inert (mineral) salt. The least effective type of the activity coefficient control, *i.e.* the isomolar system $1\text{M}-(\text{H}, \text{Na})_3\text{A}$ had to be chosen as a compromise. However, this medium cannot be taken for a medium of a constant ionic strength due to the dissociation of citric acid in several steps. Moreover, it cannot even be supposed to be a medium with neutral background electrolyte (according to Bjerrum) due to the hydrogen ion concentration range used.

However, a rather good agreement has been found between the values of the equilibrium constants of the citric acid dissociation determined in the solution of pure citric acid with the known activities of H_3A and in the isomolar system $1\text{M}-(\text{H}, \text{Na})_3\text{A}$ with the assumed constant activity coefficients of components. This agreement corroborates the assumption of the approximate constant values of the

activity coefficients in the isomolar system and justifies its use both in the citric acid extraction studies and in the metal ion extraction from the citric acid medium. During the extraction of citric acid by the solution of triaurylamine in toluene a series of $(\text{H}_3\text{A})_p(\text{TLA})_q$ complexes is formed in the organic phase. In the lower complexes $q = p + 1$ while in the higher ones $q = p$. The extraction data could be best explained by the two lowest complexes (1, 2) and (2, 3), by one complex of a medium molecular weight, represented by the (5, 6) complex, and by one higher (13, 13) complex. The fraction of the total citric acid concentration in the organic phase present in the first three complexes, which play a role in the isomolar series of $1\text{M}-(\text{H}, \text{Na})_3\text{A}$ is given in Fig. 14. The proposed set of complexes may be considered, similarly as in systems with strong mineral acids, as a simplified set substituting a continuous series of complexes between the simplest (1, 2) complex and a colloidal micelle. However, the interpretation of the experimental data by a continuous series of complexes would be very difficult with the computational facilities that were available.

The statistically "best" set of complexes shows that the colloidal micelles are formed from the lowest complex by the association of species. The type of extracted ammonium salts is different from those described in the literature, *i.e.* $(\text{BH}^+\text{A}^-)_n$, where $n \geq 1$ for strong mineral acids, and $\text{B}(\text{HA})_p$, where $p \geq 1$ for monobasic carboxylic organic acids.

The first complex $(\text{H}_3\text{A})(\text{TLA})_2$ is similar to the complex found by Pyatnitskii and Makarchuk¹¹ in the system citric acid–trioctylamine–toluene as follows from the ratio $[\overline{\text{H}_3\text{A}}]/[\overline{\text{TOA}}]$ in the equilibrium organic phase. The neutral complex $(\text{H}_3\text{A}) \cdot (\text{TLA})_3$ has not been observed even at the lowest citric acid concentrations.

The mechanism of the aggregate formation is different from the mechanism of the formation of the alkylammonium salts from mineral acids in which the ion pair

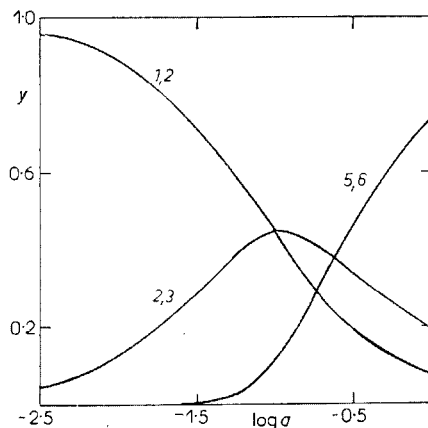


Fig. 14

The Participation of Individual Complexes on the Total Concentration of Citric Acid in the Organic Phase in $1\text{M}-(\text{H}, \text{Na})_3\text{A}$ for 5% TLA

The dependence of $y = \frac{\overline{p[(\text{H}_3\text{A})_p\text{TLA}_q]}}{\sum \overline{p[(\text{H}_3\text{A})_p\text{TLA}_q]}}$ on $\log a$ for $p = 1, 2, 5$.

dipoles of the basic complex ($\text{BH}^+ \text{A}^-$) are being aggregated. In the case of the alkylammonium salts of citric acid the species $(\text{H}_3\text{A})(\text{TLA})$, the independent existence of which has not been confirmed, are attached, at least formally, to the basic species $(\text{H}_3\text{A})(\text{TLA})_2$. The alkylammonium salts of citric acid differ by a high degree of association from weak organic carboxylic acids (acetic acid^{4,5}) or even from the medium strong acids (trichloroacetic acid⁶). Free carboxylic and hydroxyl groups in $(\text{H}_3\text{A})(\text{TLA})_2$ and $(\text{H}_3\text{A})(\text{TLA})$ contribute to the high value of the dipole moment of these species which causes the gradual increase of aggregation.

Because a continuous series of complexes $(\text{H}_3\text{A})_p(\text{TLA})_q$ with $q = p + 1$ is evidently formed, it seems improbable that the gradual growth of the alkylammonium salt aggregates could be explained only by cycles or chains connected by hydrogen bridges. The nature of the bond in the aggregates cannot be elucidated without additional information, *e.g.* from the molecular spectra.

A comparison can be made with the results of Lipovskii and Kuzina³¹ on the extraction of the oxalic acid by trioctylamine. They have found from the infrared spectra and from the cryoscopic measurements in nitrobenzene that the dimers of the ammonium salt $[(\text{H}_2\text{A})(\text{TOA})]_2$ exist in the anhydrous organic phase and that the addition of water causes dissociation to monomers. The basic complex type, *i.e.* the hydrogen salt, is similar in both systems (in the oxalic and citric acids, respectively).

The description of both systems differs in the conclusion about the size of the aggregate particles which can be explained either by the decomposition of aggregates in the polar nitrobenzene or by the fact that the size of alkylammonium salt aggregates determined by cryoscopy is usually smaller than the size determined by osmometry or by the analysis of equilibrium distribution data.

The average hydration degree of complexes decreases with the increase of their size. The (1, 2) and (2, 3) complexes contain one water molecule per one molecule of the acid while in the highest aggregates that exist in the organic phase in the equilibrium with the aqueous phase containing $> 1.5\text{M-H}_3\text{A}$ only 0.67 of water molecule is present per one molecule of the acid.

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