On Extraction with Long Chain Tertiary Amines

## XIII. The Extraction of Perchloric Acid by Trilaurylamine Dissolved in Dodecane or o-Xylene

ERIK HÖGFELDT, PIER ROBERTO DANESI* and
FOLKE FREDLUND

*Department of Inorganic Chemistry, Royal Institute of Technology,
S-100 44 Stockholm 70, Sweden*

The extraction of perchloric acid by trilaurylamine (tri-dodecyl-amine = TLA) dissolved in o-xylene as well as dodecane has been studied by the two-phase emf titration method. As in similar systems, the salt TLAHClO$_4$ forms various aggregates. In dodecane, the salt formed is rather insoluble, and precipitation occurs during titration. The data are found to be best described with the formation of monomers, dimers, and octamers in both systems. In o-xylene, a big complex (TLAHClO$_4$)$_{90}$ can be regarded as a simplified description of the aggregation processes occurring beyond the small and average size complexes. In dodecane, a considerable improvement of the fit to the data is obtained by introducing the complex (TLA)$_2$HClO$_4$. The equilibrium constants for the various complexes found are given in Table 4, and the estimated solubility products by eqns. (26 a and b).

Some batch experiments performed at high acidities in the system TLA-o-xylene-HClO$_4$ indicate extraction of a mixed acid-water complex.

In previous papers in this series [1-4] the aggregation equilibria of long-chain tertiary amine salts in both aliphatic and aromatic diluents have been studied. From these and other studies [5] it emerged that much larger aggregates are formed in aliphatic than in aromatic diluents. The degree of aggregation is also dependent upon the acid. Both emf and osmometric measurements, [1-4, 6-8] indicate an increasing degree of association of trilaurylamine salts in the order

$$Cl^- < NO_3^- < Br^- < ClO_4^-$$
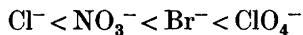
A combination of a highly aggregating solute like HClO$_4$ and an aliphatic diluent like dodecane would lead to large aggregates, and a study of these equilibria would be of interest for the understanding of the aggregation process.

---

* Laboratorio di Chimica, Casaccia, CNEN, Rome, Italy.

A similar study in an aromatic diluent would show if the same kind of species are found in both diluents. For those reasons we have studied the extraction of perchloric acid by trilaurylamine dissolved in dodecane or *o*-xylene, employing the two-phase titration method. Some batch experiments at high acidities have been performed in the *o*-xylene system. The study in dodecane has been published separately as a CNEN report.[9]

EXPERIMENTAL

Chemicals and solutions

Trilaurylamine (tridodecylamine, $(C_{12}H_{25})_3N = TLA$,) supplied by Rhône-Poulenc with only 1 % of N in form of primary or secondary amines, was the same as that used in previous studies. The amine was separated from the white precipitate present and then used as such. *o*-Xylene and dodecane, supplied by Fluka, were both checked by vapor phase chromatography and found to be 99.0 % and 99.2 %. We are indebted to Mr. Gösta Lindgren, Department of Analytical Chemistry, Royal Institute of Technology, Stockholm, for carrying out these analyses.

Solutions of TLA in both diluents were prepared on a weight basis, using calibrated volumetric flasks.

$HClO_4$, Merck *p.a.*, was used without further purification. $NaClO_4$ and $LiClO_4$ were prepared from Na_2CO_3 and Li_2CO_3 according to standard practice in our laboratory.[10,11] The concentration of the ionic medium was checked by passing a weighed amount through a strong cation exchange resin in the hydrogen form and then titrating the eluate with standard NaOH or by drying in an oven and weighing.

The following solutions were prepared: 1.00 M $NaClO_4$, 10 mM $HClO_4 + 990$ mM $NaClO_4$, 100 mM $HClO_4 + 900$ mM $NaClO_4$; 1.00 M $LiClO_4$, 1 mM $HClO_4 + 999$ mM $LiClO_4$, 10 mM $HClO_4 + 990$ mM $LiClO_4$, 100 mM $HClO_4 + 900$ mM $LiClO_4$.

The solutions containing 100 mM $HClO_4$ were standardized against spectroscopically pure Tl_2CO_3 (recrystallized twice in a platinum dish in order to remove traces of lead). The more dilute acid solutions were standardized by emf titration, employing a method outlined by Gran[12] and described elsewhere.[1] Any residual acidity in the ionic medium was determined by emf titration in a similar manner.[2] It was found preferable to keep the ionic medium $LiClO_4$ slightly acidic (pH $\sim$ 5) in order to avoid troubles deriving from dissolution of atmospheric CO_2.

LiOH, Merck *p.a.*, was used for preparing a 50 mM LiOH + 1.00 M $LiClO_4$. Its concentration was determined by titration against the 100 mM $HClO_4$ solution. All aqueous solutions were prepared from double-distilled water.

All volumetric glassware used was calibrated using double-distilled water.

For the batch experiments, various $HClO_4$-H_2O mixtures ranging from 1 – 10 M $HClO_4$ were prepared. Solutions for the Karl Fischer titrations were prepared from methanol, (containing 0.03 % H_2O), supplied by AB Kebo. Iodine, resublimed, and pyridine *p.a.* were supplied by the same company. Sulfur dioxide, obtained from a tank cylinder, was dried by passing over dehydrite. The preparation of the solutions for the Karl Fischer titration has been described elsewhere.[13]

The experimental technique

Emf measurements. The two-phase emf titration method,[14] as applied to amine systems, has been described in detail elsewhere.[1] The cells used for the emf measurements can be schematically described by

A, AgCl/990 mM $MeClO_4$, 10 mM $AgClO_4$//1000 mM (Me,H) ClO_4/G.E. (1)

↓ ↑

organic phase
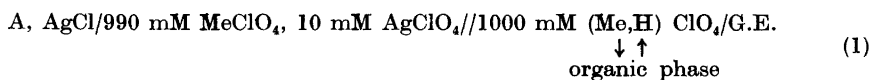
The glass electrode (G.E.) was of the Beckman blue kind (type 404948). The Ag, AgCl-electrodes were prepared according to Brown.[15] The hydrogen ion concentration [H$^+$] was evaluated from

$$E = E_0 + 59.16 \ \log \ [\text{H}^+] + j \ [\text{H}^+] \tag{2}$$

The quantities E_0 and j (< 0) were determined from separate titrations with no organic phase present. Such titrations were performed before and after each two-phase titration. If the E_0-values differed more than 0.3 mV, the corresponding two-phase titration was rejected. The emf's were measured with a Radiometer PHM4 potentiometer, calibrated against a Cambridge Vernier potentiometer.

With the dodecane system, some titrations were carried out in an atmosphere of argon, purified from O_2 in the same way as nitrogen.[10] It was found that titrations in this inert atmosphere agreed with titrations in air to within less than 0.001 Z, where Z is defined by:

$$Z = [\text{HClO}_4]_{\text{org}}/[\text{TLA}]_{\text{tot}} \tag{3}$$

With the o-xylene system, nine, and with the dodecane system, six different amine concentrations were used. They are given in Table 1.

Table 1. TLA-concentrations used, expressed in M (mol l^{-1}).

o-Xylene	Dodecane
0.00168	0.00201
0.00419	0.00397
0.00736	0.00828
0.0157	0.0200
0.0396	0.0414
0.0758	0.0774
0.1549	
0.2314	
0.3071	

Batch experiments. Samples containing 10 ml of aqueous phase and 20 ml of organic phase were shaken to equilibrium in glass-stoppered bottles in a room kept at 25.0 ± 0.3°C. After centrifuging for 5 – 10 min at 3500 rpm, aliquots were drawn from both phases and acid was determined in both phases by titrating with standard alkali, using methyl red indicator. Water in the organic phase was determined by a dead-stop titration, employing Axel Johansson's modification of the Karl Fischer method.[13,16,17]

RESULTS

The curves Z (log [H$^+$]). Using eqn. (2), [H$^+$] has been computed for each experimental point. From this value, the amount of acid in the aqueous phase was computed and subtracted from the total amount of acid added from the buret giving [HClO$_4$]$_{\text{org}}$. In Fig. 1, Z defined by (3) is plotted against log [H$^+$] = log [H$^+$] [ClO$_4^-$], since [ClO$_4^-$] = 1.00 for o-xylene and 1.00 M NaClO$_4$ as ionic medium. In Fig. 2, the same plot is given for dodecane and 1.00 M LiClO$_4$ as ionic medium, and Z-values so low that no solid precipitate has been formed, and in Fig. 3 for high Z-values, including those with a solid phase present.

Besides the appearance of a visual precipitate, the time necessary to reach equilibrium increased from about 10 – 30 min. to about 4 h when the solid
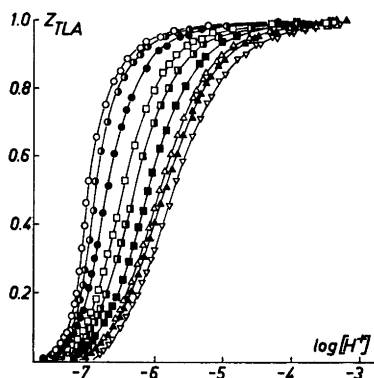
Fig. 1. Z plotted against log [H$^+$] for nine concentrations of TLA in o-xylene. ▽, 1.68 mM. ▲, 4.19 mM. △, 7.36 mM. ■, 15.7 mM. ▣, 39.6 mM. □, 75.8 mM. ●, 154.9 mM. ◑, 231.4 mM. ○, 307.1 mM.
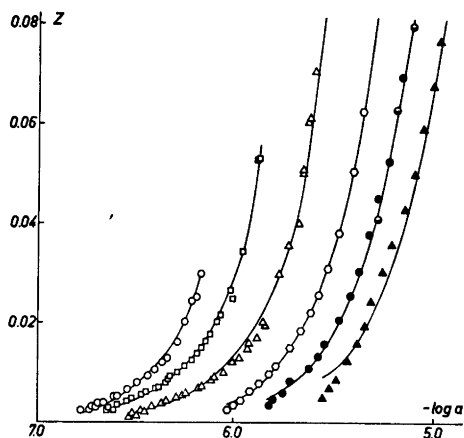
Fig. 2. Z plotted against log [H$^+$] for six concentrations of TLA in dodecane. No solid present. ▲, 2.01 mM. ●, 3.97 mM. ◓, 3.97 mM (back titration). ◯, 8.28 mM. △, 20.0 mM. □, 41.4 mM. ○, 77.4 mM.

Fig. 3. Z plotted against log [H$^+$] for six concentrations of TLA in dodecane. Solid precipitate present at the higher Z-values. Symbols as in Fig. 2. The dotted vertical lines have been computed from eqn. (27). A symbol with a small vertical line indicates formation of a visible precipitate.
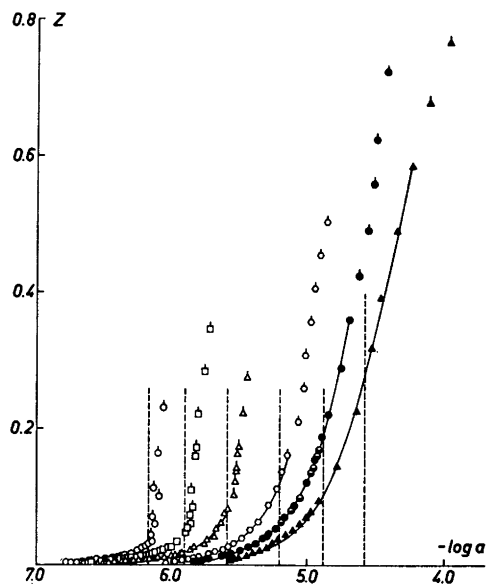
phase was formed. This slowness of approach to equilibrium could thus be used as a rather sensitive criterion for the appearance of the precipitate. The slow equilibria prevented us from carrying out the titrations up to $Z = 1$ in the dodecane system.

Table 2. Experimental data in the form log a, Z, and $(Z_{calc} - Z_{exp}) \times 10^3$ for the system TLA $-$ HClO$_4$ $-$ o-xylene. In calculating Z_{calc}, the constants given in Table 4 have been used.

Group 1
B = 0.3071 M
-7.467, 0.0373, 21.59; -7.345, 0.0700, 30.27; -7.2270, 0.1355, 43.44; -7.159, 0.2012, 74.34; -7.086, 0.3325, 49.57; -7.029, 0.4637, -7.65; -6.874, 0.6603, -43.05; -6.620, 0.8243, -38.38; -6.417, 0.8901, -24.43; -6.150, 0.9394, -12.13; -5.736, 0.9722, -0.27; -5.232, 0.9884, 2.80;

Group 2
B = 0.2314 M
-7.381, 0.0493, 15.90; -7.247, 0.0925, 19.37; -7.114, 0.1801, 17.29; -7.039, 0.2678, 12.30; -6.912, 0.4426, 9.55; -6.797, 0.6175, -40.23; -6.554, 0.7924, -35.20; -6.329, 0.8796, -24.54; -6.229, 0.9014, -16.60; -5.956, 0.9454, -6.89; -5.688, 0.9672, -0.41; -4.960, 0.9887, 5.07;

Group 3
B = 0.1549 M
-7.663, 0.0082, 8.66; -7.426, 0.0304, 10.30; -7.306, 0.0521, 11.65; -7.198, 0.0846, 10.48; -7.103, 0.1281, 6.77; -6.982, 0.2153, -5.11; -6.897, 0.3026, -20.42; -6.781, 0.4328, -25.32; -6.623, 0.6068, -25.74; -6.453, 0.7371, -21.95; -6.157, 0.8677, -12.36; -5.976, 0.9115, -6.98; -5.665, 0.9549, -1.61 -5.342, 0.9766, 1.17;

Group 4
B = 0.0758 M
-7.404, 0.0232, 4.73; -7.230, 0.0497, 2.15; -7.073, 0.0887, 1.39; -6.946, 0.1416, -3.56; -6.833, 0.2081, -11.29; -6.696, 0.3143, -23.82; -6.573, 0.4199, -27.63; -6.311, 0.6323, -19.72; -6.023, 0.7938, -4.10; -5.814, 0.8699, -0.92; -5.540, 0.9227, 7.29; -5.328, 0.9490, 7.95; -4.875, 0.9756, 9.20;

Group 5
B = 0.0396 M
-7.379, 0.0140, 7.81; -7.215, 0.0342, 3.34; -7.100, 0.0544, 0.95; -6.945, 0.0947, -1.61; -6.840, 0.1351, -4.39; -6.721, 0.1955, -8.01; -6.502, 0.3454, -15.25; -6.371, 0.4459, -14.76; -6.025, 0.6983, -15.51; -5.810, 0.7999, -5.29; -5.447, 0.9002, 6.35; -5.078, 0.9502, 9.06; -3.783, 0.9881, 9.80;

Group 6
B = 0.0157 M
-7.119, 0.0227, 11.32; -6.982, 0.0482, 3.51; -6.880, 0.0739, -2.99; -6.684, 0.1378, -8.78; -6.571, 0.1888, -10.04; -6.393, 0.2912, -8.30; -6.251, 0.3931, -9.82; -6.116, 0.4950, -11.05; -5.937, 0.6224, -11.58; -5.714, 0.7498, -8.66; -5.359, 0.8741, 0.98; -5.017, 0.9368, 4.15; -4.108, 0.9880, 4.50;

Group 7
B = 0.00736 M
-6.752, 0.0698, 7.17; -6.581, 0.1240, 1.05; -6.456, 0.1777, -1.82; -6.260, 0.2850, 0.14; -6.094, 0.3929, 6.73; -5.940, 0.5003, 11.30; -5.776, 0.6076, 16.11; -5.587, 0.7144, 18.20; -5.398, 0.7950, 20.88; -5.261, 0.8481, 13.34; -5.026, 0.9007, 15.75; -4.857, 0.9259, 16.57; -4.629, 0.9490, 16.50; -4.329, 0.9678, 14.73; -4.034, 0.9775, 13.60; -3.844, 0.9866, 7.64; -3.684, 0.9893, 6.71;

Group 8
B = 0.00419 M
-7.010, 0.0127, 20.32; -6.857, 0.0385, 10.82; -6.688, 0.0764, 1.05; -6.525, 0.1270, -7.24; -6.400, 0.1776, -11.73; -6.289, 0.2282, -9.82; -6.167, 0.3047, -16.18; -6.013, 0.4059, -14.45; -5.842, 0.5071, 5.96; -5.678, 0.6083, 15.19; -5.560, 0.6842, 9.57; -5.457, 0.7348, 12.51; -5.335, 0.7849, 16.16; -5.190, 0.8350, 17.16; -4.994, 0.8841, 18.48; -4.696, 0.9317, 17.75; -4.493, 0.9529, 15.06; -4.240, 0.9691, 12.85; -4.017, 0.9808, 8.35; -3.826, 0.9868, 6.19; -3.579, 0.9949, 1.13;

Group 9
B = 0.00168 M
-6.821, 0.0165, 30.45; -6.671, 0.0494, 18.25; -6.503, 0.0982, 3.69; -6.333, 0.1641, -10.91; -6.191, 0.2307, ~ 18.41; -6.064, 0.2966, -17.98; -5.900, 0.3955, -15.18; -5.687, 0.5274, -2.51; -5.455, 0.6592, 12.03; -5.242, 0.7574, 20.65; -5.055, 0.8220, 25.44; -4.799, 0.8853, 26.02; -4.522, 0.9288, 23.00; -4.287, 0.9525, 19.07; -4.045, 0.9684, 15.19; -3.841, 0.9776, 12.10; -3.685, 0.9829, 9.89; -3.520, 0.9888, 6.26; -3.359, 0.9927, 3.89;

Table 3. Experimental data in the form log a, $Z \times 10^4$, and $(Z_{calc} - Z_{exp}) \times 10^4$ for the system TLA $-$ HClO$_4$ $-$ dodecane (for the points used in the LETAGROP calculation). In calculating Z_{calc}, we have used the following constants (in the form $k_n \pm \sigma(k_n)$): $k_{1,1} = (2.2 \pm 1.6) \times 10^2$, $k_{2,1} = (3.9 \pm 0.1) \times 10^5$, $k_{2,2} = (1.76 \pm ;.01) \times 10^{11}$, $k_{8,8} = (1.32 \pm 0.05) \times 10^{.4}$, and the following "group constants": $k_1' = -0.0043$, $k_2' = -0.0017$, $k_3' = -0.0010$, $k_4' = -0.0017$, $k_5' = -0.0001$, $k_6' = 0.0015$. $\triangle$, points obtained from back titration.

Group 1
B = 77.4 mM
-6.735, 25, -4; -6.702, 32, -6; -6.663, 39, -5; -6.593, 53, -3; -6.548, 67, -5; -6.443, 94, 5; -6.362, 122, 9; -6.291, 162, 12; -6.189, 259, 15; -6.154, 327; -6.123, 595; -6.093, 989; -6.778, 25, -11; -6.727, 32, -10; -6.695, 39, -11; -6.612, 53, -8; -6.546, 66, -4; -6.494, 80, -2; -6.441, 94, 2; -6.407, 107, 3; -6.341, 129, 14; -6.296, 162, 8; -6.252, 203, 1; -6.216, 244, -3; -6.171, 299, 2; -6.154, 431; -6.144, 696; -6.130, 1120; -6.095, 1625; -6.056, 2296; -6.019, 2958;

Group 2
B = 41.4 mM
-6.642, 24. 3; -6.641, 30, -2; -6.548, 43, -3; -6.470, 56, -2; -6.399, 69,0; -6.348, 81, 1; -6.318, 94, -2; -6.252, 113, 1; -6.188, 139, 3; -6.142, 164, 2; -6.084, 203, 1; -6.008, 249, 22; -5.954, 344, -2; -5.878, 530, -24; -5.863, 719; -5.848, 1091; -5.824, 1589; -5.790, 2213; -5.753, 2837; -5.709, 3460; -6.612, 24, 6; -6.593, 36, -2; -6.522, 49,$-$ 5; -6.450, 62, -4; -6.384, 75, -2; -6.335, 88, -2; -6.291, 101, -1; -6.216, 126, 3; -6.164, 126, 3; -5.118, 177, 3; -6.066, 216, 1; -6.017, 267, -5; -5.956, 344, -5; -5.885, 468, 17; -5.851, 593; -5.836, 842; -5.834, 1217; -5.809, 1714; -5.778, 2213; -5.729, 2837; -5.710, 3462;

Group 3
B = 20.0 mM
-6.532, 11, 7; -6.514, 19, 1; -6.475, 26, -2; -6.370, 40, -4; -6.265, 55, -3; -6.162, 74, 1; -6.095, 92 3; -6.007, 122, 7; -5.924, 159, 15; -5.856, 203, 18; -5.728, 356, 3; -5.665, 509, -18; -5.618, 611, -25; -5.567, 813, -44; -5.525, 1071; -5.521, 1219; -5.513, 1422; -5.500, 1626; -5.456, 2235; -6.534, 11, 7; -6.500, 14, 7; -6.467, 22, 2; -6.421, 33, -3; -6.313, 44, -4; -6.294, 51, -4; -6.243, 59, -2; -6.179, 70, 0; -6.112, 85, 4; -6.051, 100, 11; -6.007, 114, 15; -5.970, 129, 18; -5.929, 148, 22; -5.888, 170, 27; -5.846, 195, 38; -5.745, 298, 35; -5.672, 400, 54; -5.664, 501, -30; -5.628, 603, -45; -5.599, 704, -58, -5.571, 806, -54; -5.523, 1065; -5.508, 1364; -5.489, 1720; -5.459, 2228; -5.429, 2735;

Group 4
B = 8.28 mM
-6.030, 26, 11; -6.000, 35, 8; -5.966, 44, 6; -5.919, 63, 0; -5.873, 79, -2; -5.827, 97, -4; -5.789, 114, -5; -5.719, 150, -5; -5.667, 185, -7; -5.614, 221, -1; -5.574, 256, 1; -5.528, 309, 0; -5.472, 380, 5; -5.405, 504, -1; -5.354, 624, -6; -5.280, 870, -26; -5.175, 1358, 10; -5.138, 1602, 30; -5.072, 2092; -5.016, 2580; -5.016, 3072; -4.974, 3560; -4.935, 4050; -4.896, 4538; -4.854, 5026;

Group 5
B = 3.97 mM
-5.826, 35, 17; -5.804, 47, 10; -5.766, 60, 5; -5.718, 84, -5. -5.623, 109,3; -5.577, 133, 0; -5.545, 158, -6; -5.476, 206, -8; -5.418, 255, -7; -5.374, 304; -10; -5.324, 378, -21; -5.280, 451, -29; -5.224, 524, 0; -5.160, 693, -25; -5.094, 861, -3; -5.009, 1198, -19; -4.942, 1538, -21; -4.886, 1875, -4; -4.837, 2212, 27; -4.752, 2890, 105; -4.691, 3602, -5; -4.615, 4239; -4.549, 4910; -4.507, 5586; -4.441, 6235; -4.309, 7243, $\triangle -5.280$, 408; $\triangle -5.183$, 626; $\triangle -5.107$, 796; $\triangle -5.053$, 973: $\triangle -5.008$, 1165; $\triangle -4.969$, 1340; $\triangle -4.950$, 1423; $\triangle -4.925$, 1601; $\triangle -4.906$, 1680;

Group 6
B = 2.01 mM
-5.554, 50, 41; -5.521, 68, 33; -5.494, 86, 25; -5.432, 123, 15; -5.385, 158, 5; -5.342, 193, -2; -5.314, 244, -32; -5.254, 302, -37; -5.209, 356, -42; -5.146, 427, -28; -5.095, 498, -14; -5.050, 588, -15; -5.001, 675, 11; -4.972, 765, 1; -4.906, 942, 32; -4.779, 1438, 7; -4.710, 1940, -43; -4.627, 2431, 16; -4.534, 3175, 3; -4.455, 3911, -41; -4.343, 4889, -10; -4.228, 5848, 4; -4.101, 6783; -3.950, 7669;

The reversibility of the reaction was checked in the dodecane system by a back titration with the $LiOH - LiClO_4$ solution. The results of this titration are shown in Figs. 2 and 3, and it is evident that the forward and back titrations agree to within the experimental accuracy (~ 0.001 Z).

In Tables 2 and 3 the values of Z, ($\log [H^+]$), are listed.

Average composition of complexes. From Figs. $1-3$ is seen that the curves do not coincide indicating the possible formation of polynuclear complexes. In order to obtain information about the composition of these complexes, the averages $\bar{p}$ and $\bar{q}$ were evaluated. Since ionic dissociation is negligible in the diluents under study,[18] the reactions can be written

$$q\text{TLA}(org) + p\text{H}^+(aq) + p\text{ClO}_4^-(aq) \rightleftharpoons (\text{TLA})_p(\text{HClO}_4)_p(org) \qquad (4)$$
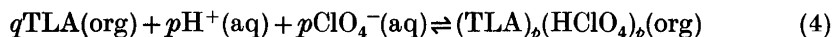
Application of the law of mass action to (4) with the assumption of ideal behaviour in both phases (dilute solutions in the organic phase, ionic medium in the aqueous phase) gives

$$[(\text{TLA})_q(\text{HClO}_4)_p]_{org} = k_{p,q}[\text{TLA}]_{org}{}^q[\text{H}^+]^p[\text{ClO}_4^-]^p \qquad (5)$$

where square brackets indicate concentrations, and the aqueous phase is left without subscript.

The averages $\bar{p}$ and $\bar{q}$ defined by

$$\bar{p} = \sum p[(\text{TLA})_q(\text{HClO}_4)]_p / \sum[\text{TLA})_q(\text{HClO}_4)_p] \qquad (6\text{ a})$$

$$\bar{q} = \sum q[(\text{TLA})_q(\text{HClO}_4)_p] / \sum[(\text{TLA})_q(\text{HClO}_4)_p] \qquad (6\text{ b})$$

can be evaluated from the data $Z(\log [H^+])$, the only assumption necessary being the validity of the equilibrium law in its simple stoichiometric form.[19] The application to amine systems has been discussed in detail elsewhere.[1,20]

In Figs. 4 and 5, $\bar{p}$ is plotted against $\bar{q}$ for the two systems. The calculations have been performed with the computer program MESAK.[21] In both cases, most of the data cluster along the line $\bar{p} = \bar{q}$, indicating the main complexes to be $(\text{TLAHClO}_4)_n$ as found to be common for the complexing between long-chain tertiary amines and strong acids.[1-4, 6] For the highest amine concentrations, $\bar{p} = \bar{q}$ in Fig. 4, indicating more than one acid per amine. This must be attributed to experimental errors, because all curves tend towards $Z = 1$ in Fig. 2. On the other hand, the possibility of mixed complexes between base and acid form $\bar{q} = \bar{p}$ is indicated in Fig. 5.
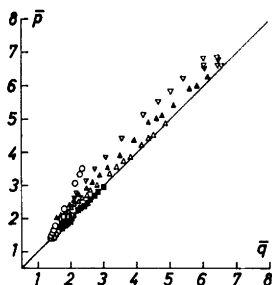

Fig. 4. $\bar{p}$ plotted against $\bar{q}$ for TLA in *o*-xylene. Symbols as in Fig. 1.
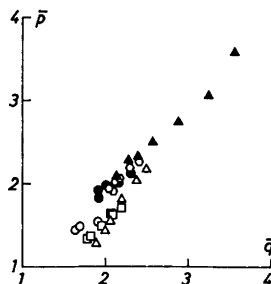
Fig. 5. $\bar{p}$ plotted against $\bar{q}$ for TLA in dodecane. Symbols as in Fig. 2.

Table 4. Complexes indicated and their equilibrium constants for the extraction of perchloric acid by TLA dissolved in *o*-xylene or dodecane. $t = 25°C$.

	o-Xylene				Dodecane			
Complex	$\log(k_{n,n} \pm 3\sigma(k_{n,n}))$	$\log k_n$	$\log k_0$	$\log k$	Complex	$\log (k_{n,n} \pm 3\sigma(k_{n,n}))$	$\log k_n$	$\log k_0$	$\log k$
TLAHClO$_4$	5.46 ± 0.09	—	—	—	TLAHClO$_4$	2.34 (2.78)	—	—	—
(TLAHClO$_4$)$_2$	13.88 ± 0.06	2.96	-2.96	8.42	(TLAHClO$_4$)$_2$	11.25 ± 0.01	6.57	-6.57	8.91
(TLAHClO$_4$)$_8$	59.89 (60.17)	16.21	-2.32	7.78	(TLAHClO$_4$)$_8$	54.12 ± 0.05	34.40	-4.91	7.40
(TLAHClO$_4$)$_{90}$	699.49 (700.04)	258.01	-2.90	7.80	(TLA)$_2$HClO$_4$	$\log k_{2,1} =$ 5.59 ± 0.03	—	—	—
	$\sigma(Z) = 0.017$					$\sigma(Z) = 0.0023$			

If $\sigma(k) > 0.2$ k, only the best value for $\log k$ and the maximum value $\log (k + 3\sigma(k))$ are given.

Evaluation of possible complexes. The experimental data have been treated with LETAGROPVRID,[22-25] a computer program designed to find, in the present case, the minimum of the error square sum:

$$U = \sum_1^n (Z_{exp} - Z_{calc})^2 \tag{7}$$

the summation taken over all experimental points.

For both systems, many different combinations between some $30 - 40$ complexes have been tried. In Table 4 are given the two combinations giving the lowest error square sum. The first column gives the composition of the complex, and the second the value of $\log [k_{n,n} \pm 3\sigma(k_{n,n})]$, where $k_{n,n}$ is defined according to (3) for $p = q = n$. In both systems, monomers, dimers, and octamers were found to give the best fit. In dodecane, the aggregation is so large that monomers are too scarce to give a good value for $k_{1,1}$, and in xylene the octamer is not prominent enough to give a good value for $k_{8,8}$. On the other hand, the octamer survived competition with many other complexes. In order to get a good value for $k_{1,1}$ in dodecane one has to go to lower amine concentrations than those studied here, which is extremely difficult.

The complex (TLAHClO$_4$)$_{90}$ was obtained by trying systematically bigger and bigger complexes together with the three smaller ones. It was found that the error square sum decreased until it reached a constant value at about $n = 90$. The (90,90) complex is thus only indicative of a tendency towards formation of large aggregates. It is possible that all complexes exist from monomer to very large aggregates in the system, the description with a few small complexes and one very large being a simplification. On the other hand, a description with all possible complexes requires some simplifying assumption, the simplest being that the addition of a monomer to a complex releases a constant amount of free energy. With such an assumption we get

$$k_{n,n} = k_0 k_n \tag{8}$$

and a simple geometric series to sum, where k is the constant ratio between two consecutive constants, and k_0 taking care of all other effects. Of further interest are the association constants of the various aggregates. The third column in Table 4 gives the logarithm of the association constant k_n for the reaction

$$n \; \text{TLAHClO}_4 \rightleftharpoons (\text{TLAHClO}_4)_n \tag{9}$$
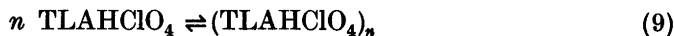
in the organic phase.

Log k_n is obtained from

$$\log \; k_n = \log \; k_{n,n} - n \; \log \; k_{1,1} \tag{10}$$

In order to obtain rough estimates of k_0 and k, they can be computed from the following two expressions:

$$-\log \; k_0 = \frac{1}{n-1} \log \; k_n \tag{11 a}$$

$$\log \; k = \frac{1}{n-1} \log \; (k_{n,n}/k_{1,1}) \tag{11 b}$$

which are obtained from (8) and (10).

Columns four and five of Table 4 give the value for k_0 and k, obtained from (11). It is seen that the aggregation constants in dodecane are roughly the square of those in o-xylene, and that the simple geometric series seems to fit better in xylene than in dodecane.

In dodecane, the complex $(\text{TLA})_2\text{HClO}_4$ is found to improve the fit to such an extent that a rather well-defined equilibrium constant is obtained. Excluding this complex gives systematic deviations much larger than the experimental accuracy. In xylene, such a complex was rejected, $i.e.$ it did not improve the fit and $k_{2,1} = 0$. Recently, a similar (2,1)-complex has been found with nitric acid in octane and dodecane [26] and might be indicative of a tendency towards self-solvation in these non-polar solvents. This complex exists in appreciable amounts only at low Z-values, and systematic errors giving rise to the same effect are difficult to exclude. A possibility might be appreciable amounts of amine in the aqueous phase. Below, estimates are given for the distribution coefficients of TLA and TLAHClO$_4$ which hardly support that assumption. In Table 4, the standard deviation in Z, $\sigma(Z)$, is given for the two systems, showing the fit between experimental and calculated $Z(\log [\text{H}^+])$-curves. The fit is acceptable for both systems.

In order to illustrate how the various complexes vary with acidity, the fraction $(\alpha_{p,q})$ of all amine present in various complexes $(\text{TLA})_q(\text{HClO}_4)_p$ is plotted against $\log [\text{H}^+] [\text{ClO}_4^-]$ in Figs. 6 and 7 for two different amine concentrations in the two diluents. The calculations have been performed with the computer program HALTAFALL [27] and the constants given in Table 4. From Fig. 6 is evident that at low amine concentrations in o-xylene, only the monomer-dimer equilibrium has to be considered. At high amine concentrations, the distribution of the various complexes is constant and independent of acidity both in o-xylene, where no precipitate has been observed, as well as in dodecane, where precipitation occurs. From Fig. 7 is seen that the amount of monomer is always small, even negligible at high amine concentrations. That is the reason why the equilibrium constant for
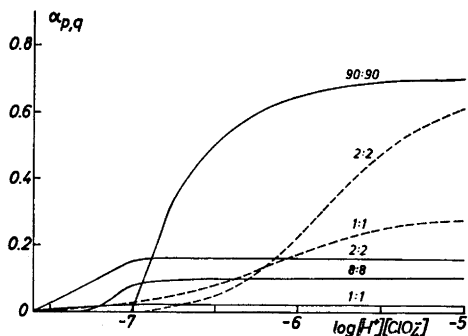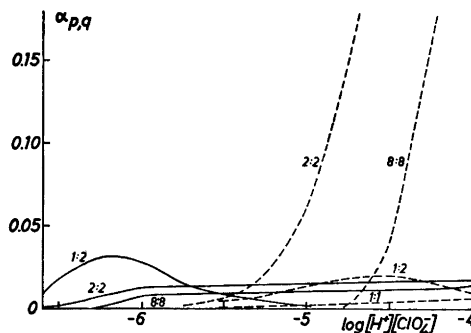
Fig. 6. The fraction $\alpha_{p,q}$ of all amine present in the complex $(TLA)_q(HClO_4)_p$ plotted against log $[H^+]$ $[ClO_4^-]$ for the system TLA-*o*-xylene-HClO$_4$.
———, 0.2314 M TLA.
— — —, 0.00419M TLA.

Fig. 7. The fraction $\alpha_{p,q}$ of all amine present in the complex $(TLA)_q(HClO_4)_p$ plotted against log $[H^+]$ $[ClO_4^-]$ for the system TLA-dodecane-HClO$_4$.
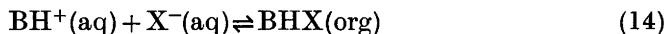———, 0.0774 M TLA.
— — —, 0.0020 M TLA.

that complex is uncertain. The 1:2 complex is always a small fraction of all amine present, increasing slightly with total amine concentration.

The distribution of amine between the two phases. Consider the two distribution equilibria (B = amine base)

$$B(aq) \rightleftharpoons B(org) \tag{12}$$

$$D_B = [B]_{org}/[B] \tag{13}$$

$$BH^+(aq) + X^-(aq) \rightleftharpoons BHX(org) \tag{14}$$

$$D_{BHX} = [BHX]_{org}/[BH^+] \, [X^-] \tag{15}$$

where X stands for the anion present.

For the acid-base reaction in the aqueous phase we have

$$BH^+ \rightleftharpoons H^+ + B \tag{16}$$

$$k_a = [H^+][B]/[BH^+] \tag{17}$$

From (13), (15), (17), and (5) for $p = q = 1$, the following relation is obtained:

$$\log k_{1,1} = \log D_{BHX} - \log D_B + pk_a \tag{18}$$

Dyrssen [28] has recently estimated D_B and D_{BHX} for nitrates and chlorides of tertiary ammonium salts. For primary, secondary, and tertiary aliphatic amines he found

$$\log D_B = 0.6n - A \tag{19}$$

where n = number of carbon atoms in the molecule, and A 2.3 in aromatic solvents and 1.4 in chloroform. For the acidity constant he used $pk_a = 10.6$ as a reasonable average.

Recently Smulek and Siekierski [29] obtained $D_{TOAHCl} = 170$ for TOA = trioctylamine in heptane and 8 M HCl. We have found log $k_{1,1} \sim 2.3$ both for

HNO_3 [4] and $HClO_4$ (Table 4) in aliphatics. If we assume log $k_{1,1} = 2.3$ for HCl also, we get

$$\log D_{BHX} = 0.6 \; n - 12.2 \quad (X = Cl^-, \; NO_3^-, \; ClO_4^-) \tag{20}$$

which gives for TLA $(n = 36)$

$$\log D_{BHClO_4} = 9.4$$

Even if this value is too high by 10^3, the amount of $TLAHClO_4$ in an aqueous phase in equilibrium with 0.1 M in the organic phase is smaller than 1 μM, which is negligible.

For the base form we get from (18) and (20), with $pk_a = 10.6$,

$$\log D_B = 0.6n - 3.9 \; \text{(aliphatics)},$$

which for TLA gives log $D_B = 17.7$, and certainly negligible amounts of base in the aqueous phase. A direct attempt to evaluate D_B by shaking to equilibrium with water and analysing by the Gran method gave $D_B \geq 10^7$. For $TLAHClO_4$ in o-xylene we obtain from (19) with $A = 2.3$ and log $k_{1,1} = 5.5$ (Table 2)

$$\log D_{BHClO_4} = 0.6 \; n - 7.4 \tag{22}$$

For $TLAHClO_4$ this gives log $D_{BHClO_4} = 14.2$. This value is so high that the extraction of $TLAHClO_4$ in water from aromatic solvents can be neglected. Bucher and Diamond [30] reported $[TLAHClO_4]_{aq} = 1 \times 10^{-5}$ M, which can only be regarded to give an upper limit to the true solubility, the method of analysis not being sensitive enough.

The solid phase. Solid $TLAHClO_4$ was prepared by shaking TLA in dodecane with the 100 mM $HClO_4 + 900$ mM $LiClO_4$ solution, the latter amount in slight excess of the amount required for stoichiometric neutralization. The white precipitate formed was filtered off, crystallized several times from acetone, and finally dried over P_2O_5. The equivalent weight was determined by dissolving in acetone and titrating with standard NaOH. The determined value was 634 ± 12 (average of 6 determinations), thus agreeing to within 2 % with the composition $TLAHClO_4$.

For the solubility of $TLAHClO_4$ we have

$$TLAHClO_4(s,org) \rightleftharpoons TLA(org) + H^+(aq) + ClO_4^-(aq) \text{ and} \tag{23}$$
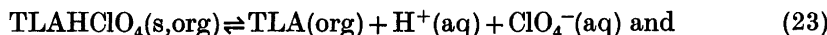
$$k_s = [TLA]_{org}[H^+][ClO_4^-] = u \tag{24}$$

when setting the activity of $TLAHClO_4(s)$ equal to unity.

At the appearance of $TLAHClO_4(s)$, the quantity u must be constant. For these points, when a precipitate had formed, the quantity u was computed, the product $[H^+][ClO_4^-]$ obtained from the emf measurement and $[TLA]_{org}$ from
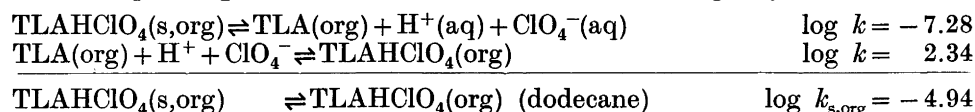
$$[TLA]_{org} = [TLA]_{tot} \; (1 - Z) \tag{25}$$

which is obtained from the material balances for amine and acid with $p = q = n$, which assumption was valid to better than 0.5 % for the points where the solid phase appeared because $(TLA)_2HClO_4$ had practically disappeared at these Z-values (*cf.* Fig. 7). From about 50 experimental points

$$k_s = 5.3 \times 10^{-8} \quad (\log\ k_s = -7.28 \pm 0.03) \tag{26 a}$$

This value is about two powers of ten lower than for TLAHNO$_3$ in both aromatic and aliphatic diluents,[31,26] reflecting the stronger tendency towards aggregation of TLAHClO$_4$. For TLAHClO$_4$ in o-xylene, computation of u, according to (24) for Z-values close to unity, we find

$$\log\ k_s = -7.74 \pm 0.03 \tag{26 b}$$

The aqueous phase can be eliminated in the following way:

TLAHClO$_4$(s,org) $\rightleftharpoons$ TLA(org) + H$^+$(aq) + ClO$_4^-$(aq)	$\log\ k = -7.28$
TLA(org) + H$^+$ + ClO$_4^-$ $\rightleftharpoons$ TLAHClO$_4$(org)	$\log\ k = 2.34$

TLAHClO$_4$(s,org) $\rightleftharpoons$ TLAHClO$_4$(org) (dodecane) $\qquad \log\ k_{s,org} = -4.94$

In the same way we find $\log k_{s,org} = -2.28$ in o-xylene, showing the much higher solubility of TLAHClO$_4$ in o-xylene as compared with dodecane.

The solubility constants found can be used to predict whether precipitation will occur. In the HALTAFALL calculations, the solubility products given by (26 a and b) were included. For o-xylene, the data predict no precipitation in the whole concentration and acidity range studied. For dodecane, the predicted values are in agreement with Fig. 2. It is very simple to obtain a rough estimate at what acidity precipitation can be expected to occur. We replace [TLA]$_{org}$ in (24) with [TLA]$_{tot}$ and find

$$\log\ [\text{H}^+][\text{ClO}_4^-] = \log[\text{H}^+] = -7.28 - \log[\text{TLA}]_{tot} \tag{27}$$

The values for $\log[\text{H}^+][\text{ClO}_4^-]$ predicted from (27) are given as dotted vertical lines in Fig. 3. As seen, the predictions are in agreement with experimental observation, except at the two lowest amine concentrations where the approximation [TLA]$_{org} \sim$ [TLA]$_{tot}$ at the point of precipitation becomes poor.
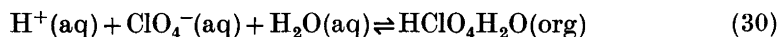
An interesting task is to study the influence of diluent as well as amine structure on these solubilities, in order to get methods for predicting the possibility of precipitation. We hope our studies of various amine systems will be of help towards that end.

Batch experiments. In Fig. 8, Z and Z_{H_2O} are plotted against the stoichiometric molarity (C_{HClO_4}) of acid in the aqueous phase for the system TLA-o-xylene-HClO$_4$. It is seen that the coextraction of water as well as the extraction of excess acid is small. A mixed acid-water complex is obviously extracted. However, the effect is small, and no certain conclusions can be drawn about the mechanism of extraction. A simple description fitting the data fairly well are the following two distribution equilibria:

$$\text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{org}) \tag{28}$$
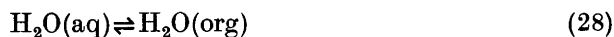
$$k = 0.20 = [\text{H}_2\text{O}]_{org}/[\text{TLA}]_{tot}\{\text{H}_2\text{O}\} = Z_{H_2O}/\{\text{H}_2\text{O}\}_{org} \tag{29}$$

where {H$_2$O} is the activity of water in the aqueous phase and

$$\text{H}^+(\text{aq}) + \text{ClO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{HClO}_4\text{H}_2\text{O}(\text{org}) \tag{30}$$

$$\log k = \log(Z - 1) - \log\{\text{H}^+\}\{\text{ClO}_4^-\}\{\text{H}_2\text{O}\} = -7.65 \pm 0.15 \tag{31}$$
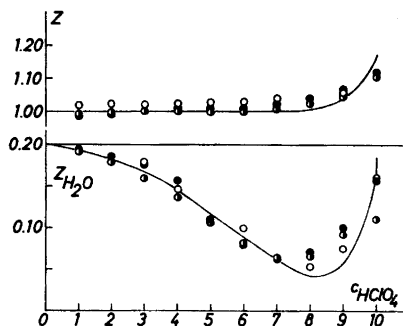
Fig. 8. Z (upper half) and Z_{H_2O} (lower half) plotted against the stoichiometric molarity of perchloric acid in the aqueous phase (C_{HClO_4}). O, 77.7 mM. ●, 155.5 mM. ◖, 234.0 mM. The curves have been computed from eqns. (29) and (31).

The fulldrawn curves in Fig. 8 have been computed from (29) and (31). These equations can be used to predict the amount of acid and water extracted by TLAHClO$_4$, but no certain claim can be made as to the nature of the species involved. This situation is illustrated by Warnqvist [32] who found that several different descriptions can fit similar data equally well, a large enough range of extraction to obtain a unique description being very difficult to achieve.

DISCUSSION

As would be expected by considering the low dielectric constant and inert character of dodecane *versus* the relatively large dipole moment of TLAHClO$_4$, the polymerisation goes so far that for the highest amine concentrations

Table 5. Values for log k_2 and log k_8 of (TLAHClO$_4$)$_2$ and (TLAHClO$_4$)$_8$ in various diluents. $t = 25°C$.

Constant	Diluent				
	Benzene	Toluene	o-Xylene (this work)	Cyclohexane	Dodecane (this work)
log k_2	2.38 (7) 2.27 (8) 2.26 (30) 2.36 (33)	2.23 (33)	2.96	3.25 (7)	6.57
log k_8	14.00 (7) 14.08 (8) 14.08 (33)	13.95 (33)	16.21	20.17 (7)	34.40

Number within parenthesis is the number in the reference list.

precipitation occurs even at low Z-values. The tendency towards aggregation is also illustrated by the much larger aggregation constants in dodecane than in xylene. Of the complexes suggested, the two species $(TLAHClO_4)_2$ and $(TLAHClO_4)_8$ receive some support from osmometric measurements in benzene,[7,8] toluene,[33] and cyclohexane by two different groups of investigators. Besides, the extraction data of Bucher and Diamond,[30] using benzene as solvent, also point to the formation of monomers, dimers, and perhaps higher aggregates. In Table 5, log k_2 and log k_8 from the various studies are compared. From Table 5 is evident that cyclohexane falls between aliphatic and aromatic hydrocarbons, while the aggregation in o-xylene should be expected to be closer to that in benzene, indicating the possibility that water ($cf.$ Fig. 8) might slightly enhance the aggregation. A direct comparison with a dry and a wet system is desirable for that purpose. Work in that direction is now in progress in our laboratory.

REFERENCES

1. Högfeldt, E. and Fredlund, F. *Trans. Royal Inst. Technol.*, No. 226 (1964).
2. Högfeldt, E. and Fredlund, F. *Trans. Royal Inst. Technol.*, No. 227 (1964).
3. Högfeldt, E. and de Jesus Tavares, M. *Trans. Royal Inst. Technol.*, No. 228 (1964).
4. Högfeldt, E., Fredlund, F. and Rasmusson, K. *Trans. Royal Inst. Technol.*, No. 229 (1964).
5. Hardy, J. C. and Miles, J. H. *At. Energy Res. Estab. (Gr. Brit.) Memo* 1141 (1963).
6. Lodhi, M. A. *Arkiv Kemi* 27 (1967) 309.
7. Markovits G. and Kertes, A. S. In Dyrssen, D., Liljenzin, J. O. and Rydberg, J. *Solvent Extraction Chemistry*, North-Holland Publ. Co. Amsterdam 1967, p. 390.
8. Orlandini, F., Danesi, P. R., Basol, S. and Scibona. G. *Ibid.* p. 408.
9. Danesi, P. R. and Högfeldt, E. RT/CHI (66) 38, CNEN, Rome 1966.
10. *Some Laboratory Methods*, Mimeograph, Inorganic Chemistry, Royal Inst. Technol., Stockholm, Sweden.
11. Biedermann, G. and Ciavatta, L. *Acta Chem. Scand.* 15 (1961) 1347.
12. Gran, G. Analyst 77 (1952) 661.
13. Högfeldt, E. and Fredlund, F., *Trans. Royal Inst. Technol.*, No. 224 (1964).
14. Högfeldt, E. *Acta Chem. Scand.* 6 (1952) 610.
15. Brown, A. S. *J. Am. Chem. Soc.* 56 (1934) 646.
16. Johansson, A. *Svensk Papperstid.* 50 No. 11B (1947) 124.
17. Johansson, A. *Private communication* 1961.
18. Fredlund, F. and Högfeldt, E. *Unpublished results.*
19. Sillén, L. G. *Acta Chem. Scand.* 15 (1961) 1981.
20. Högfeldt, E. and Fredlund, F. *Acta Chem. Scand.* 17 (1964) 1085.
21. Sillén, L. G. and Ingri, N. *Private communications* 1962.
22. Sillén, L. G. *Acta Chem. Scand.* 16 (1962) 159.
23. Ingri, N. and Sillén, L. G. *Acta Chem. Scand.* 16 (1962) 173.
24. Sillén, L. G. *Acta Chem. Scand.* 18 (1964) 1085.
25. Ingri, N. and Sillén, L. G. *Arkiv Kemi* 23 No. 10 (1965) 97.
26. Högfeldt, E. In Kertes-Marcus, *Solvent Extraction Research*, Wiley, New York 1969, p. 157.
27. Ingri, N., Kakolowicz, W., Sillén, L. G. and Warnqvist, B. *Talanta* 14 (1967) 1261.
28. Dyrssen, D. *Svensk Kem. Tidskr.* 77 (1965) 387.
29. Smulek, W. and Siekierski, S. *J. Inorg. Nucl. Chem.* 24 (1962) 1651.

30. Bucher, J. and Diamond, R. W. *J. Phys. Chem.* **69** (1965) 1565.
31. Högfeldt, E. *Svensk Kem. Tidskr.* **76** (1964) 290.
32. Warnqvist, B. *Acta Chem. Scand.* **21** (1967) 1353.
33. Danesi, P. R., Magini, M. and Scibona, G. In Kertes — Marcus, *Solvent Extraction Research*, Wiley, New York 1969, p. 185.