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On Extraction with Long Chain Tertiary Amines

XII. The Extraction Equilibria in the System 2.75 M (H,Li)NO_3-Trilauryl-amine-Toluene

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The distribution of HNO_3 in the system 2.75 M (H,Li)NO_3-trilaurylamine (B)-toluene was measured in the range of $-\log[H^+]_{aq} = 8$ to 1 by two-phase emf titration, and in the range 1 to 0 by batch experiments. The total concentration of B was varied between 0.00437 and 0.368 M. Neglecting possible non-ideality of the organic phase at high $[B]_{tot}$, the extraction equilibria were described assuming complexes of the general formula $B_q(HNO_3)_p$. The best fit to the experimental data was found (using the computer program LETAGROPVRID) for the following set of complexes (p,q): (1,1), (2,2), (3,3), (50,50), (2,1), (6,4), (6,5). The corresponding equilibrium constants are given in Table 4.

Trialkylammonium salts (R_3NHA) of strong mineral acids (HA) dissolved in low dielectric organic solvents seem to be aggregated in the concentration range pertinent for the extraction of metals. The species formed are generally of a type $(R_3NHA)_n$.[1] At higher acidities, more acid molecules are added, forming, *e.g.*, $R_3N(HA)_2$,[1,2] but little is known whether these species form aggregates or not, although one investigation indicates formation of aggregates.[3]

In the present work, the equilibria in the system 2.75 M (H,Li)NO_3-trilaurylamine(B)-toluene were studied, with the aim, among others, to reinterpret the data given by Lloyd and Mason [4] on the distribution of uranium with the same extracting system.

EXPERIMENTAL

Chemicals and solutions. Lithium nitrate, Mallinckrodt, A.R., nitric acid, Merck *p.a.*, and toluene, Merck *p.a.*, were used without further purification. The purity of toluene

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was checked by VPC, and found to be 99.2 % pure. Trilaurylamine (tridodecylamine, B), Rhône-Poulenc, was freed from the white precipitate by centrifugation. Trilaurylammonium nitrate was prepared by adding B dropwise into a ~0.5 M HNO_3 under vigorous stirring, until the acidity of the aqueous phase was pH ~ 2. The precipitate formed was then washed three times with water, dried in a desiccator, once recrystallized from hexane, and dried in air at 40°C.

Solutions of 2.75 M (0.001, 0.01, and 0.1 M H; Li)NO_3, 2.75 M HNO_3, and 2.75 M $LiNO_3$ were prepared by mixing from stock solutions of $LiNO_3$ and HNO_3. The concentration of $LiNO_3$ was calculated from the weight of added stock solution, and the two stronger acid solutions were standardized with $KHCO_3$ and Tl_2CO_3. The two weaker acid solutions were standardized by emf-titrations according to the Gran method.[5] The amount of amine present in the organic phase was approximately given by the amount weighed out. However, the purity of the amine has been found to be approximately 99 %.[5] For that reason, a better value for $[B]_{tot}$ was obtained by curve fitting to the uppermost part of the titration curve, using normalized curves.[6]

When equilibrating the solution of $BHNO_3$ in toluene with 0.001 M HNO_3, 2.75 M $LiNO_3$, the acidity in the aqueous phase decreased, indicating the presence of free amine in the organic phase. By titration with acid and fitting to the experimental titration curves, the organic phase was found to contain 1.24 ± 0.02 % free amine.

The amount of $BHNO_3$ in the organic phase was found by titrating with standard alkali, using phenolphthalein as indicator in a solution diluted with an equal volume of acetone.

Experimental technique. The experimental technique used for two-phase titration was substantially that described by Högfeldt and Fredlund.[5]

The experimental data in the highest acidity range were obtained by batch experiments. 50 ml of both phases were vigorously mixed for 1 h with a magnetic stirrer. The initial aqueous phase contained a certain excess of acid, so that the composition of the equilibrium aqueous phase was (2.75 ± 0.03) M (H,Li)NO_3. The phases were separated by centrifugation, and the acidity in both phases was determined with standard NaOH, using for the aqueous phase mixed methyl red-bromophenol green as indicator, and for the organic phase phenolphthalein. The organic phase was diluted before titration with an equal volume of acetone, *p.a.*

RESULTS

The experimental data are given in Table 1, and graphically in Fig. 1. For every amine concentration, the data in Table 1 are given as log $[H^+]$,Z, where Z is defined by

$$Z = [HNO_3]_{org}/[B]_{tot} \qquad (1)$$

In Fig. 1, Z is plotted against log $[H^+]$ for the amine concentrations studied: 0.0044 M, 0.0199 M, 0.0502 M, 0.121 M, 0.246 M, and 0.368 M. For log $[H^+] < -1$, the data have been obtained by two-phase titrations, and for log $[H^+] > -1$, by batch experiments. In the range of overlap, the two methods agree up to log $[H^+] = -1$; above that value the emf-method is too uncertain to be used. At about this acidity, the glass electrodes usually began to behave irreversibly.

TREATMENT OF DATA

The data were treated in a similar way as described in preceding papers in this series (see, *e.g.*, Ref. 5).

Table 1. Distribution of HNO_3 in the system 2.75 M $(H,Li)NO_3$-trilaurylamine-toluene The corresponding values of ($\log[H^+]_{aq}$, Z) are given.

Two-phase titration

$[B]_{tot} = 0.00437$ M

−7.342, 0.00430; −7.411, 0.00538; −7.269, 0.00763; −7.277, 0.00875;
−7.164, 0.0131; −7.068, 0.0197; −6.993, 0.0252; −6.924, 0.0305;
−6.851, 0.0373; −6.796, 0.0436; −6.706, 0.0546; −6.704, 0.0549;
−6.625, 0.0664; −6.564, 0.0771; −6.386, 0.111; −6.310, 0.133;
−6.189, 0.168; −6.104, 0.200; −6.011, 0.235; −5.945, 0.278;
−5.869, 0.303; −5.793, 0.345; −5.744, 0.370; −5.680, 0.413;
−5.624, 0.437; −5.563, 0.480; −5.518, 0.505; −5.343, 0.614;
−5.242, 0.664; −5.120, 0.727; −5.108, 0.729; −4.988, 0.784;
−4.968, 0.793; −4.828, 0.841; −4.802, 0.850; −4.574, 0.906;
−4.213, 0.958; −3.658, 0.989; −3.293, 0.998; −3.127, 0.999_6;

$[B]_{tot} = 0.0199$ M

−7.314, 0.00984; −7.208, 0.0148; −7.091, 0.0222; −6.963, 0.0296;
−6.873, 0.0395; −6.796, 0.0493; −6.675, 0.0642; −6.566, 0.0789;
−6.464, 0.104; −6.371, 0.123; −6.305, 0.148; −6.219, 0.173;
−6.065, 0.248; −6.004, 0.278; −5.889, 0.352; −5.813, 0.402;
−5.768, 0.429; −5.665, 0.503; −5.592, 0.553; −5.512, 0.605;
−5.467, 0.631; −5.345, 0.705; −5.284, 0.733; −5.127, 0.806;
−5.046, 0.835; −4.982, 0.857; −4.875, 0.885; −4.782, 0.907;
−4.615, 0.935; −4.442, 0.957; −4.049, 0.983; −3.579, 0.996;

$[B]_{tot} = 0.0502$ M

−7.389, 0.00965; −7.336, 0.0118; −7.181, 0.0196; −7.014, 0.0313;
−6.826, 0.0508; −6.738, 0.0626; −6.657, 0.0781; −6.547, 0.103;
−6.500, 0.120; −6.388, 0.160; −6.314, 0.184; −6.300, 0.200;
−6.228, 0.239; −6.162, 0.280; −6.113, 0.304; −6.101, 0.320;
−6.045, 0.360; −5.993, 0.400; −5.949, 0.424; −5.938, 0.440;
−5.886, 0.480; −5.835, 0.519; −5.780, 0.560; −5.732, 0.582;
−5.727, 0.600; −5.668, 0.640; −5.605, 0.680; −5.538, 0.720;
−5.475, 0.774; −5.457, 0.760;
−5.367, 0.800; −5.262, 0.840; −5.173, 0.864; −5.127, 0.880;
−4.941, 0.919; −4.765, 0.943; −4.628, 0.960; −3.656, 0.996;

$[B]_{tot} = 0.1210$ M

−7.771, 0.00165; −7.811, 0.00168; −7.697, 0.00333; −7.671, 0.00336;
−7.549, 0.00656; −7.534, 0.00662; −7.441, 0.00979; −7.355, 0.0131;
−7.252, 0.0178; −7.172, 0.0228; −7.056, 0.0309; −6.980, 0.0390;
−6.863, 0.0519; −6.806, 0.0639; −6.630, 0.101; −6.584, 0.122;
−6.430, 0.185; −6.354, 0.238; −6.239, 0.318; −6.128, 0.421; −6.006, 0.517;
−5.835, 0.650; −5.812, 0.670; −5.612, 0.782; −5.607, 0.786; −5.438, 0.853;
−5.392, 0.865; −5.252, 0.902; −5.186, 0.916; −5.066, 0.936; −4.963, 0.949;
−4.848, 0.960; −4.676, 0.973; −4.439, 0.985; −4.289, 0.989;

$[B]_{tot} = 0.246$ M

−7.820, 0.00195; −7.683, 0.00389; −7.583, 0.00598; −7.514, 0.00798;
−7.424, 0.0110; −7.348, 0.0139; −7.271, 0.0180; −7.169, 0.0239;
−7.061, 0.0319; −6.997, 0.0398; −6.900, 0.0524; −6.863, 0.0589;
−6.796, 0.0728; −6.716, 0.101; −6.626, 0.135; −6.550, 0.183; −6.457, 0.257;
−6.393, 0.326; −6.295, 0.442; −6.195, 0.528; −6.157, 0.569; −6.170, 0.571;
−6.116, 0.609; −6.102, 0.647; −6.072, 0.650; −6.026, 0.690; −5.971, 0.731;
−5.906, 0.772; −5.832, 0.812; −5.732, 0.853; −5.698, 0.850; −5.597, 0.893;
−5.531, 0.916; −5.227, 0.956; −4.970, 0.974; −4.987, 0.976; −4.950, 0.977;
−4.696, 0.987; −4.338, 0.994; −4.213, 0.996;

Table 1. Continued.

$[B]_{tot} = 0.368$ M

−7.800, 0.00268; −7.705, 0.00407; −7.587, 0.00670; −7.478, 0.00943;
−7.369, 0.0134; −7.281, 0.0174; −7.172, 0.0267; −7.103, 0.0294;
−7.024, 0.0403; −6.910, 0.0553; −6.801, 0.0979; −6.741, 0.109; −6.601, 0.193;
−6.473, 0.330; −6.439, 0.382; −6.380, 0.443; −6.356, 0.484; −6.322, 0.525;
−6.322, 0.549; −6.288, 0.567; −6.258, 0.608; −6.222, 0.636; −6.204, 0.683;
−6.179, 0.691; −6.138, 0.737; −6.102, 0.765; −6.045, 0.795; −6.008, 0.819;
−5.927, 0.850; −5.849, 0.877; −5.751, 0.905; −5.631, 0.929; −5.617, 0.932;
−5.524, 0.945; −5.416, 0.956; −5.217, 0.973; −5.005, 0.982; −4.926, 0.986;
−4.461, 0.995; −4.263, 0.996;

$[B]_{tot} = 0.0201$ M

−3.757, 0.996; −2.750, 1.003; −2.455, 1.005; −2.280, 1.007; −2.163, 1.009;
−1.998, 1.011; −1.884, 1.012; −1.737, 1.018; −1.403, 1.034; −1.221, 1.049;
−1.007, 1.081;

$[B]_{tot} = 0.1225$ M

−3.758, 0.997; −3.183, 1.000; −2.864, 1.002; −2.572, 1.004; −2.426, 1.005;
−2.236, 1.008; −2.052, 1.012; −1.900, 1.017; −1.715, 1.032; −1.475, 1.045;
−1.222, 1.073; −1.002, 1.113;

$[B]_{tot} = 0.368$ M

−4.180, 0.998; −3.585, 1.000; −3.064, 1.002; −2.800, 1.005; −2.568, 1.008;
−2.377, 1.012; −2.167, 1.018; −1.908, 1.032; −1.722, 1.043; −1.502, 1.065;
−1.338, 1.087; −1.117, 1.126;

Batch experiments

$[B]_{tot} = 0.0201$ M

−0.991, 1.090; −0.599, 1.167; −0.217, 1.289; 0.003, 1.401;

$[B]_{tot} = 0.1225$ M

−0.991, 1.119; −0.595, 1.214; −0.215, 1.333; 0.003, 1.409;

$[B]_{tot} = 0.368$ M

−1.065, 1.130; −0.593, 1.238; −0.193, 1.346; 0.046, 1.430;

The general reaction for the extraction of HNO_3 can be written

$$q\mathrm{B}_{\mathrm{org}} + p\mathrm{H}^+ + p\mathrm{NO_3}^- \rightleftharpoons \mathrm{B}_q(\mathrm{HNO_3})_{p\ \mathrm{org}} \tag{2}$$

and the equilibrium constant of the complex (p,q) is defined as

$$k_{p,q} = [(\mathrm{B})_q(\mathrm{HNO_3})_p]_{\mathrm{org}}/[\mathrm{B}]_{\mathrm{org}}{}^q[\mathrm{H}^+]^p[\mathrm{NO_3}^-]^p \tag{3}$$

Using the computer program MESAK [7] (whose principles are given by Sillén [8]), the average values of $\bar{p}$ and $\bar{q}$ were calculated:

$$\bar{p} = \sum pC_{p,q}/\sum C_{p,q} \tag{4}$$

$$\bar{q} = \sum qC_{p,q}/\sum C_{p,q} \tag{5}$$

where $C_{p,q} = [\mathrm{B}_q(\mathrm{HNO_3})_p]$. The plot of $\bar{p}$ as a function of $\bar{q}$ is given in Fig. 2. The first part of most of the curves follows rather close the line $\bar{p} = \bar{q}$. The points which correspond to the values of $Z > 1.0$ start to deviate in the direction of $\bar{p} > \bar{q}$. The curves in this part of the diagram do not, however, coincide, indicating that complexes with various p/q ratios are formed.

The evaluation of the system was therefore attempted in three steps:

(1) The region of lowest [B](≤ 0.0502 M B) and $Z \leq 1.0$, where complexes of small $p = q$, and a definite composition can be assumed to exist.[1]

(2) Using the complexes found in region (1), the calculations were extended for all concentrations of B and $Z \leq 1.0$, in order to find the higher aggregates.

(3) Finally, in the region of $Z > 1.0$, complexes with $p > q$ were searched for.

The calculations were made, using the computer program LETAGROPVRID,[9] which searches for the set of values $(p,q,k_{p,q})$ that would minimize the error square sum defined by

$$U = \sum_{1}^{n_p} (y_{\text{calc}} - y_{\text{exp}})^2 \tag{6}$$

(n_p is the number of experimental points). In the present case, $y = Z$. As the calculations in different parts of this paper were made using different n_p, for easier comparison of the significance of various sets of $(p,q,k_{p,q})$, the standard deviations in Z ($\sigma(Z)$) are given. The equilibrium constants are given as log $[k_{p,q} \pm 3\sigma(kp,q)]$. If, however, $\sigma(k_{p,q}) > 0.2\ k_{p,q}$, then in parenthesis following the value of log $k_{p,q}$, only $\log[k_{p,q} + 3\sigma(k_{p,q})] - \log k_{p,q}$ is indicated.

(1) The region of $[B]_{\text{tot}} \leq 0.0502$ M, $Z < 1.0$

In this region, various combinations of complexes (1,1), (2,2), (3,3), and (4,4), were tried. In Table 2, the standard deviations in Z for the combinations tried are given, along with the $k_{p,q}$. Out of all combinations tried, only the rather high value of $\sigma(Z)$ permits one to reject the combination (1,1), (2,2), but the others seem to have equal significance.

Table 2. The complexes tried to fit the data on the extraction of HNO_3 in the system 2.75 M $(H,Li)NO_3$-trilaurylamine-toluene in the region of $[B]_{\text{tot}} \leq 0.0502$ M.

Complexes (p,q)	$\log[k_{p,q} \pm 3\sigma(k_{p,q})]$	$\sigma(Z)$
(1,1)	4.994 ± 0.017	0.00689
(2,2)	11.829 ± 0.034	
(1,1)	5.065 ± 0.008	0.00525
(3,3)	18.729 ± 0.029	
(1,1)	5.045 ± 0.019	0.00492
(2,2)	11.29 (+0.26)	
(3,3)	18.58 ± 0.15	
(1,1)	5.032 ± 0.016	0.00484
(2,2)	11.59 ± 0.11	
(4,4)	25.35 ± 0.15	

(2) The region of $Z<1.0$

Using all three sets of complexes (*i.e.* (1,1), (3,3); (1,1), (2,2), (3,3); and (1,1), (2,2), (4,4)), calculations were extended to find higher aggregates. Two series of calculations were made:

(a) with the earlier found values of $k_{p,q}$ for the small complexes and varying only the $k_{p,q}$ for the larger complexes in the range $[B]_{tot} \geq 0.121$ M and $Z > 1.0$;

(b) varying all $k_{p,q}$ and using all data for $Z < 1.0$.

If the complexes and their $k_{p,q}$ given in Table 2 do describe the species really present, then in both series of calculations, aggregates of similar size ought to be found. The results of the calculations are given in Figs. 3 – 5.

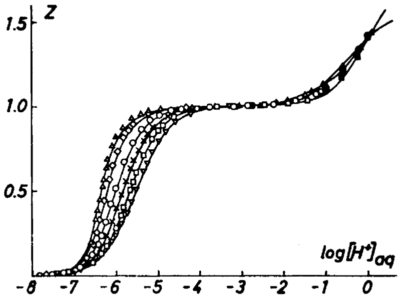

Fig. 1. Z as a function of log $[H^+]_{aq}$ for various concentrations of B. Open symbols: data obtained by two-phase titration. Filled symbols: data obtained by batch experiments. ▽, 0.00437 M B. □, ■ 0.0199 M B. ×, 0.0502 M B. ○, ●, 0.1210 M B. ◇, 0.246 M B. △, ▲, 0.368 M B.

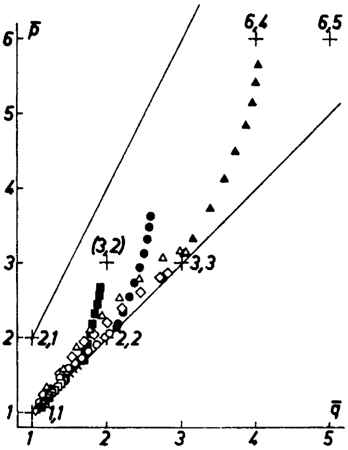

Fig. 2. The average numbers of HNO_3 ($\bar{p}$) and B ($\bar{q}$) per complex $B_q(HNO_3)_p$ for various concentrations of B. ▽, 0.00437 M B. □, ■, 0.0199 M B. ×, 0.0502 M B. ○, ●, 0.1210 M B. ◇, 0.0246 M B. △, ▲, 0.368 M B. Filled symbols refer to data in the range $Z > 1.0$.

For the aggregate of the size $p(=q) = 8 - 70$, the respective values of $\sigma(Z)$ and $\sigma(k_{p,q})/k_{p,q}$ for both series are given.

First of all, it seems that the combinations of complexes (1,1), (2,2), (4,4), (p,q) are to be rejected, because both series give a minimum of the $\sigma(Z) = f(p)$ curve at rather different values of p. The best combination of complexes seems to be (1,1), (2,2), (3,3), (p,q), with $p \simeq 50$. The values of $k_{p,q}$ for this combination and also for (1,1), (3,3), (50,50), which is the best in the combination (1,1), (3,3), (p,q), are given in Table **3**.

The curves drawn in Fig. 1 are calculated for the combination of $(p,q,k_{p,q})$, mentioned above. With increasing $[B]_{tot}$, increasing systematic deviations of the calculated curves from the experimental points can be observed. The

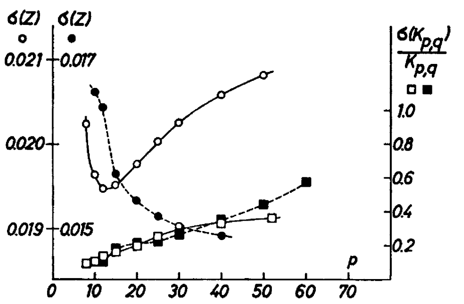

Fig. 3. The results of computation for the set of complexes (1,1), (2,2), (4,4), (p,q). Open symbols: data for $[B]_{tot} \geq 0.121$ M, $Z < 1.0$, and only $K_{p,q}$ was varied. Filled symbols: all data for $Z < 1.0$, all $k_{1,1}$, $k_{2,2}$, $k_{4,4}$, and $k_{p,q}$ were varied. Standard deviations in Z (○, ●, and the left hand scale), and the relative standard deviations in $k_{q,p}$ ($\sigma(k_{p,q})/(k_{p,q})$) (□, ■, and the right hand scale) are given as a function of p ($=q$).

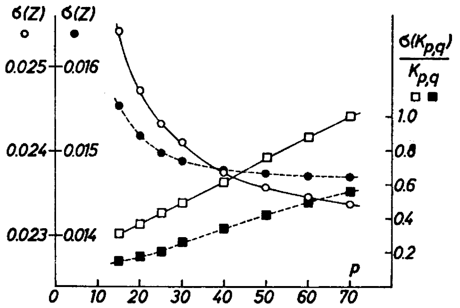

Fig. 4. The result of computation for the set of complexes (1,1), (2,2), (3,3), (p,q). Open symbols: data for $[B]_{tot} \geq 0.121$ M, $Z < 1.0$, and only $k_{p,q}$ was varied. Filled symbols: all data for $Z < 1.0$, all $k_{1,1}$, $k_{2,2}$, $k_{3,3}$, and $k_{p,q}$ were varied. Standard deviations in Z (○, ●, and the left hand scale), and the relative standard deviations in $k_{p,q}$ ($\sigma(k_{p,q})/k_{p,q}$) (□, ■, and the right hand scale) are given as a function of p ($=q$).

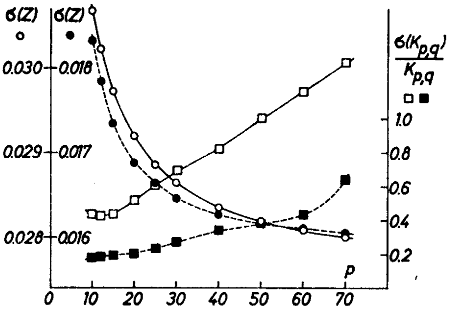

Fig. 5. The results of computation for the sets of complexes (1,1), (3,3), and (p,q). Open symbols, data for $[B]_{tot} < 0.121$ M, $Z < 1.0$, and only $k_{p,q}$ was varied. Filled symbols: all data for $Z < 1.0$, all $k_{1,1}$, $k_{3,3}$, and $k_{p,q}$ were varied. Standard deviations in Z (○, ●, and the left hand scale), and the relative standard deviations in $k_{p,q}$ ($\sigma(k_{p,q})/k_{p,q}$) (□, ■, and the right hand scale) are given as a function of p ($=q$).

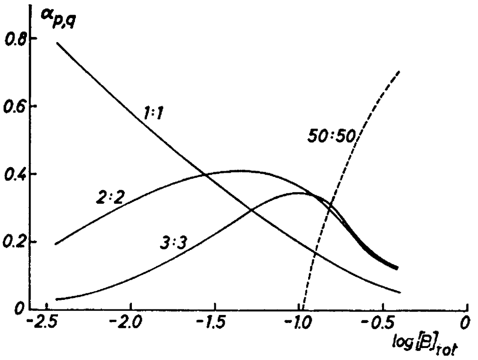

Fig. 6. The fraction $\alpha_{p,q}$ of all amine present in the complex $B_q(HNO_3)_p$ plotted against $\log[B]_{tot}$ at $\log[H^+] = -2.25$. The curve for the 50:50 complex is dashed because of its formal character.

possibility that these deviations are caused by some species with $p > q$ – as might be indicated by the middle part of some curves in Fig. 2 – seems to be excluded for two reasons:

Table 3. Complexes, their equilibrium constants, and $\sigma(Z)$ for the extraction of HNO_3 in the system 2.75 M $(H,Li)NO_3$-trilaurylamine-toluene, in the region of $Z \leq 1.0$.

Complexes (p,q)	$\log[k_{p,q} \pm 3\sigma(k_{p,q})]$	$\sigma(Z)$
(1,1)	5.015 ± 0.041	0.0147
(2,2)	11.68 ± 0.19	
(3,3)	18.19 (+0.21)	
(50,50)	330.85 (+0.28)	
(1,1)	5.087 ± 0.021	0.0162
(3,3)	18.577 ± 0.044	
(50,50)	330.65 (+0.33)	

(a) The curves in Fig. 2 approach again the line $p=q$ near $Z=1$.

(b) As the subsequent calculations have shown, the contribution of complexes $p>q$ is negligible in the pertinent region. It is possible that these deviations are partly due to non-ideality in the organic phase for the two highest amine concentrations.

(3) The region of $Z>1.0$

From the information obtained in Fig. 2, it can be deduced that at higher acidities in the aqueous phase, complexes with $p>q$ are formed in the organic phase. Various combinations of complexes in the range $1.0<p/q<2.0$, $p<20$ were tested, and some of the best combinations are given in Table 4. They are also shown in Fig. 2.

In Fig. 6, the fraction $\alpha_{p,q}$ of all amine present in the complex $B_q(NHO_3)_p$ is plotted against $\log\,[B]_{tot}$ at $\log\,[H^+]=-2.25$. The calculations have been performed with the computer program HALTAFALL[10] and the constants given in Table 4. As seen, only at the highest amine concentrations it is necessary to take the large complexes into account. However, these concentrations are those used in the practical work.

The solubility product. From the data around $Z=1$, an estimate of the equilibrium constant for aggregates so large that they can be formally treated as a separate phase can be made. Consider the reaction

$$BHNO_3(s)(org) \rightleftharpoons B(org) + H^+ + NO_3^- \tag{7}$$

We define the activity of B $HNO_3(s)$ as unity, and obtain

$$k_s = [B]_{org}[H^+][NO_3^-] \tag{8}$$

$[B]_{org}$ is obtained from the relationship

$$[B]_{org} = [B_{tot}](1-Z) \tag{9}$$

which is obtained from the material balance expressions for acid and amine when only complexes of the 1:1 composition need to be taken into account.

Table 4. Complexes, their equilibrium constants, and $\sigma(Z)$ for the extraction of HNO_3 in the system 2.75 M $(H,Li)NO_3$-trilaurylamine-toluene for $Z=0-1.4$.

Complexes (p,q)	$\log[k_{p,q} \pm 3\sigma(k_{p,q})]$	$\sigma(Z)^a$
(1,1)	5.01 (not varied)	0.0118
(2,2)	11.68 (not varied)	
(3.3)	18.19 (not varied)	
(50,50)	330.33 (+0.45)	
(2,1)	4.50 ± 0.08	
(6,4)	25.66 ± 0.10	
(6,5)	32.54 ± 0.14	
(1,1)	5.01 (not varied)	0.0115
(2,2)	11.68 (not varied)	
(3.3)	18.19 (not varied)	
(50,50)	330.29 (+0.61)	
(2,1)	4.46 ± 0.22	
(3,2)	11.16 (+0.64)	
(6,4)	25.62 ± 0.16	
(6,5)	32.50 ± 0.08	
(1,1)	5.01 (not varied)	0.0112
(2,2)	11.68 (not varied)	
(3.3)	18.19 (not varied)	
(50,50)	330.30 (+0.53)	
(2,1)	4.59 ± 0.09	
(5,4)	25.58 ± 0.26	
(6,4)	25.32 (+0.30)	
(12,10)	66.29 ± 0.34	
(12,8)	52.30 (+0.37)	

[a] $\sigma(Z)$ is given only for data $Z \geq 1.0$.

The following value was obtained:

$$\log k_s = -7.14 \pm 0.06$$

Combination of this value with the value $\log k_{1,1} = 5.45$ for the formation of $BHNO_3$, given in Table 4 gives

$$\log k'_s = -1.69$$

for the reaction

$$B\ HNO_3(s)(org) \rightleftharpoons B\ HNO_3(org) \tag{10}$$

In some systems, k_s' is so low that a visible precipitate appears, *e.g.* $TLAHClO_4$ in dodecane.[11] In the present system, the solubility is sufficiently high to prevent precipitation.

DISCUSSION

The results in the present paper are typical of what we find in many of the systems studied. A few small complexes of the 1:1 composition are formed stepwise. In order to simplify the calculations and not introduce too many constants, the large complex can be regarded as some kind of average, illustrating that aggregation continues beyond the smaller complexes. On the other hand, attempts to fit similar data with a geometric series give a poorer fit.[12] It cannot be decided from the present information, however, whether only some small and one large complex (micelle) are formed or the whole series of complexes from 1:1 up to $\approx$ 50:50 coexist in this and similar systems.

It is interesting to note that in the range $Z > 1$, the curves do not coincide, indicating the formation of species other than those with the 1:1 composition. A similar result was recently obtained by Kojima *et al.*[13] in the system TOA-benzene-HCl-H_2O, where non-coinciding curves could be interpreted in a manner similar to that given in this paper. It is possible that this effect is more general than hitherto believed, provided the experiments are carried out carefully enough to observe the effect.

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