

## On the Aggregation of the Complex between Nitric Acid and Trilaurylamine Dissolved in Octane and *m*-Xylene

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The extraction of nitric acid by trilaurylamine (TLA) dissolved in octane or *m*-xylene has been investigated by using two-phase emf-titrations. The results can be described by the following reactions



where  $n$  is large in alifatic diluents like octane but moderate in aromatic diluents like xylene.

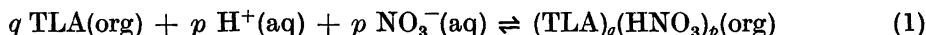
Preliminary values for the first two complexes in *m*-xylene and the ionic medium 1.00 M  $(\text{Na}^+, \text{H}^+)\text{NO}_3^-$  in the aqueous phase are as follows:

$$k_{1,1} = (1.62 \pm 0.04) \times 10^4 \text{ M}^{-2}$$

$$k_{2,2} = (3.20 \pm 0.11) \times 10^{10} \text{ M}^{-5}$$

At the Seventh International Conference on Coordination Chemistry (7 ICC) we communicated some preliminary results on the mechanism for the extraction of nitric acid by trilaurylamine (tri-dodecylamine, TLA) dissolved in octane or *m*-xylene.<sup>1a,b</sup> These results have been useful in attempts to evaluate the mechanism for the extraction of technetium<sup>2</sup> as well as uranyl nitrate.<sup>3</sup> As they may be of some interest also to others a brief account is given below together with some additional results for TLA in *m*-xylene. The experimental technique used, two-phase emf-titrations, was described in 1952 by Högfeldt and Dyrssen,<sup>4,5</sup> and has been discussed in detail in a recent paper by Högfeldt and Fredlund.<sup>6</sup>

Since we can assume the ionic dissociation to be negligible in the organic phase, the reactions studied can be written as follows



Application of the law of mass action to (1) gives, with the assumption of ideal behavior in the organic phase:

$$[(\text{TLA})_q(\text{HNO}_3)_p]_{\text{org}} = K_{p,q} \cdot [\text{TLA}]_{\text{org}}^q \{\text{H}^+\}_{\text{aq}}^p \cdot \{\text{NO}_3^-\}_{\text{aq}}^p \quad (2)$$

where [ ] denotes concentration and { } activity. The ionic medium used was 1 M  $(\text{Na}^+, \text{H}^+)\text{NO}_3^-$  and the activity coefficients of  $\text{H}^+$  and  $\text{NO}_3^-$  in the

aqueous phase can be assumed to be constant. For that reason the activity product  $\{H^+\} \cdot \{NO_3^-\}$  in the aqueous phase can be replaced by  $[H^+] \cdot [NO_3^-]$ , the product of the molarities of  $H^+$  and  $NO_3^-$  and eqn. (2) can be written

$$[(TLA)_q(HNO_3)_p]_{org} = k_{p,q} [TLA]_{org}^q [H^+]_{aq}^p \cdot [NO_3^-]_{aq}^p \quad (3)$$

where

$$k_{p,q} = K_{p,q} y_{H^+}^p y_{NO_3^-}^p \quad (4)$$

and  $y_{H^+}$  and  $y_{NO_3^-}$  are the molar activity coefficients of  $H^+$  and  $NO_3^-$  in the ionic medium used.

Reaction (1) may be treated formally as a special case of the general formation of complexes  $A_p B_q$  from the two reactants A and B. For the reaction



$$[A_p B_q] = \beta_{p,q} a^p \cdot b^q \quad (6)$$

where  $\beta_{p,q}$  = equilibrium constant,  $a = [A]$ ,  $b = [B]$ .

In the present case  $A = HNO_3$  and  $B = TLA$ . As seen from a comparison of (3) and (6), we may write, formally  $[H^+] \cdot [NO_3^-] = a$ ;  $[TLA]_{org} = b$ .

Furthermore  $[A]_{tot} = A = [HNO_3]_{org}$ ,  $[B]_{tot} = B = [TLA]_{tot}$ .

If  $Z$  = average number of A per B =  $[HNO_3]_{org}/[TLA]_{tot}$ , then  $BZ = A - a_o$ , the amount of bound A. It is convenient to plot  $Z$  against  $\pm \log a$ , in this case against  $-\log [H^+] \cdot [NO_3^-]$ . This is done in Fig. 1 for six concentrations of TLA in *m*-xylene, ranging from 0.1 % to 5 % TLA.

In Fig. 1 it is seen that the curves  $Z(-\log [H^+] [NO_3^-])$  do not coincide which indicates the possible formation of polynuclear species, *i.e.* species in which

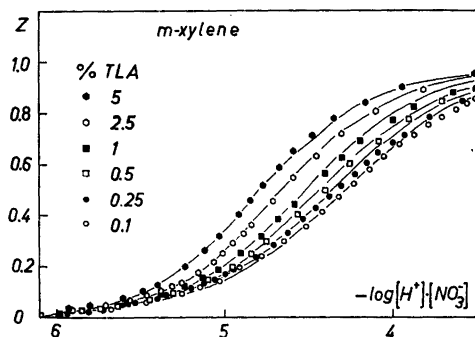


Fig. 1.  $Z$  plotted against  $-\log([H^+][NO_3^-])$  for six concentrations of TLA in *m*-xylene. The curves are calculated assuming the formation of  $TLA \cdot HNO_3$  and  $(TLA \cdot HNO_3)_2$  with the constants  $k_{1,1} = 1.7 \times 10^4 M^{-2}$  and  $k_{2,2} = 3.5 \times 10^{10} M^{-5}$ .

$q$  is greater than one. Analogous results were obtained for TLA in octane. In order to evaluate the composition of the species formed, a general method developed by Sillén<sup>7</sup> has been applied to the data. The derivation below follows that in Ref.<sup>7</sup>

The material balance for B gives

$$B = [B] + \sum q[A_p B_q] = b + \sum q\beta_{p,q} a^p \cdot b^q \quad (7)$$

The material balance for A gives

$$A = a_o + \sum p\beta_{p,q} a^p \cdot b^q \text{ or } BZ = A - a_o = \sum p\beta_{p,q} a^p \cdot b^q \quad (8)$$

The functions  $S$  and  $R$  are now introduced

$$S = \sum \beta_{p,q} a^p \cdot b^q \quad (9)$$

$$BR = b + S \quad (10)$$

where  $S$  is the sum of the concentrations of all complexes and  $BR$  is that of all species containing B.

The average number of A-molecules per complex,  $\bar{p}$ , is defined by

$$\bar{p} = \frac{\sum p[A_p B_q]}{\sum [A_p B_q]} = \frac{\sum p\beta_{p,q} a^p \cdot b^q}{\sum \beta_{p,q} a^p \cdot b^q} = \frac{BZ}{S} \quad (11)$$

where  $[A_p B_q]$  is the concentration of the complex  $A_p B_q$  and the summation is made over all complexes  $A_p B_q$  present in the system. Analogously the average number of B-molecules per complex,  $\bar{q}$ , is defined by

$$\bar{q} = \frac{\sum q[A_p B_q]}{\sum [A_p B_q]} = \frac{\sum q\beta_{p,q} a^p \cdot b^q}{\sum \beta_{p,q} a^p \cdot b^q} = \frac{(B-b)}{S} \quad (12)$$

Differentiation of (10) gives, after rearrangement and use of (7), (8), and (9), the latter differentiated with respect to  $a$  and  $b$ .

$$d(BR) = B dR + R dB = B d \ln b + BZ d \ln a \quad (13)$$

This gives:

$$d(\ln b - R) = R d \ln B - Z d \ln a \quad (14)$$

(14) is a total differential and by use of the properties of partial derivatives one gets from (14)

$$\left(\frac{\partial R}{\partial Z}\right)_B = \left(\frac{\partial \ln a}{\partial \ln B}\right)_Z = -D \quad (15)$$

From data  $Z(\log a)$ , cf. Fig. 1,  $D$  can be evaluated. Integration of (15) at constant  $B$  gives with the proper integration constants

$$1 - R = \text{const} + \int D dZ = Z(\bar{q} - 1)/\bar{p} \quad (16)$$

Integration of (14) gives (17) after the following operations: adding  $-\ln B$  to both sides, including  $-\ln B$  on the right side into the integration constant, inserting (16), and rearranging.

$$\ln(b/B) = \text{const} - \int D dZ - \int Z d \ln a = \ln [1 - (Z\bar{q}/\bar{p})] \quad (17)$$

The only assumption made is that the law of mass action is obeyed in its simple form, *i.e.*, as given in eqn. (3) above. In Fig. 2  $\bar{p}$  is plotted against  $\bar{q}$  for octane and in Fig. 3 for *m*-xylene. From these plots it is seen that the points cluster along the line  $\bar{p} = \bar{q}$  indicating that the complexes formed are of the type  $(\text{TLA} \cdot \text{HNO}_3)_n$ .

In order to illustrate how  $\bar{p}$  ( $= \bar{q}$ ) changes during a titration  $\bar{p}$  is plotted against  $-\log([\text{H}^+] \cdot [\text{NO}_3^-])$  for ten concentrations of TLA in octane in Fig. 4

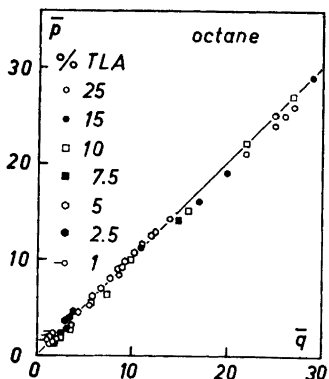


Fig. 2.  $\bar{p}$  plotted against  $\bar{q}$  for the system TLA-octane- $\text{HNO}_3$ - $\text{H}_2\text{O}$ .

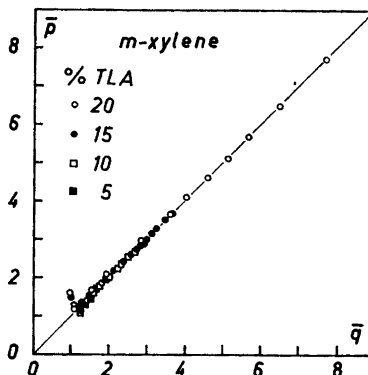


Fig. 3.  $\bar{p}$  plotted against  $\bar{q}$  for the system TLA-*m*-xylene- $\text{HNO}_3$ - $\text{H}_2\text{O}$ .

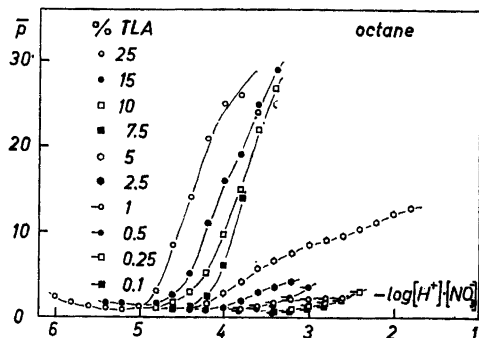


Fig. 4.  $\bar{p}$  plotted against  $-\log([\text{H}^+][\text{NO}_3^-])$  for ten concentrations of TLA in octane.

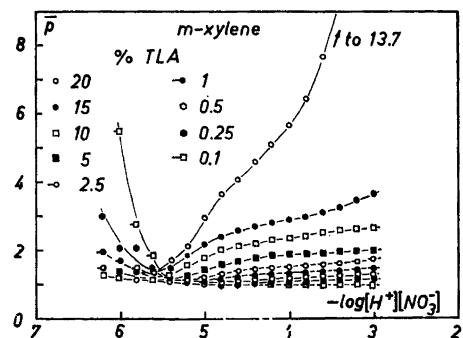


Fig. 5.  $\bar{p}$  plotted against  $-\log([\text{H}^+][\text{NO}_3^-])$  for nine concentrations of TLA in *m*-xylene.

and for nine concentrations of TLA in *m*-xylene in Fig. 5. In Fig. 4 it is seen that for amine concentrations  $> 5\%$  the aggregation rapidly increases to about 20–30. In Fig. 5, if we disregard values below  $[\text{H}^+] \cdot [\text{NO}_3^-] = 10^{-5.8}$  where the experimental uncertainty is large and  $\bar{p}$  and  $\bar{q}$  are sensitive to the choice of the integration constant in (17), it is seen that the aggregation is

moderate up to 15 % TLA. Above that concentration extensive aggregation sets in as illustrated by the curve for 20 % TLA. From Fig. 5 it is seen that up to 5 % TLA in *m*-xylene  $\bar{p}$  (and  $\bar{q}$ ) approach 2. In this range the data could be fitted by a monomer-dimer equilibrium and for these two complexes the following values were obtained by curve-fitting<sup>1b</sup>

$$\begin{aligned} k_{1,1} &= 1.7 \times 10^4 \text{ M}^{-2} \\ k_{2,2} &= 3.5 \times 10^{10} \text{ M}^{-5} \end{aligned} \quad (18a,b)$$

A computer refinement using the program LETAGROP worked out by Sillén and Ingri<sup>8</sup> for obtaining a least-squares fit to the data gave the following results (the deviations given are  $\pm \sigma$ )

$$\begin{aligned} k_{1,1} &= (1.62 \pm 0.04) \times 10^4 \text{ M}^{-2} \\ k_{2,2} &= (3.20 \pm 0.11) \times 10^{10} \text{ M}^{-5} \end{aligned} \quad (19a,b)$$

As indicated in Fig. 3 larger aggregates are formed and in the final refinement this has to be taken into account. For that reason the constants given in (18) and (19) must be used with caution, they can only be regarded to give a first approximation to the behavior in the solutions under consideration.

The two systems considered above as well as the systems:

TLA-*o*-xylene-HNO<sub>3</sub>-H<sub>2</sub>O; TLA-dodecane-HNO<sub>3</sub>-H<sub>2</sub>O and TLA-*o*-xylene-HCl-H<sub>2</sub>O will be discussed in detail in publications to appear elsewhere.<sup>6, 9-11</sup>

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