

## On Extraction with Long Chain Tertiary Amines

### VIII. Extraction of Trichloroacetic Acid and Water by Trilaurylamine Dissolved in *o*-Xylene

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From distribution measurements and the determination of the water content of the organic phase, trichloroacetic acid (HA) seems to be extracted by *o*-xylene in the form of  $\text{HA}\cdot\text{H}_2\text{O}$  and some larger species, probably  $\text{H}_2\text{A}_2(\text{H}_2\text{O})_3$ . The extraction of HA by trilaurylamine (TLA) solutions in *o*-xylene has been studied in two systems. By two-phase titrations the extraction of HA from 1 M (H, Na)A has been studied and the complexes  $\text{TLA}\cdot\text{HA}$  and  $\text{TLA}(\text{HA})_2$  are found in the organic phase. The distribution of HA and the water content of the organic phase has been further studied in the range  $C_{\text{HA,aq}} = 0.08$  M–4 M. Besides the complexes  $\text{TLA}\cdot\text{HA}$  and  $\text{TLA}(\text{HA})_2$  the data indicate  $\text{TLA}(\text{HA})_3(\text{H}_2\text{O})$  and some higher complex such as  $\text{TLA}(\text{HA})_7(\text{H}_2\text{O})_7$ . Equilibrium constants for the formation of the complexes have been determined employing computer methods.

From the freezing point data found in the literature, the mean ionic activity coefficients of trichloroacetic acid and the activity of water in aqueous solutions of trichloroacetic acid have been calculated for the range  $C_{\text{HA}} = 0$ –5.0 M.

In previous papers of this series the extraction of various mineral acids by trialkylamines, especially by trilaurylamine (TLA), has been reported.<sup>1-7</sup> By two-phase emf-titrations it has been found that, for strong acids at low acidities, complexes of general formula  $(\text{TLA}\cdot\text{HA})_n$  are formed in the organic phase. On the other hand weak acids like acetic acid<sup>8</sup> seem to form only mononuclear complexes  $\text{TLA}(\text{HA})_n$ . At high acidities all are extracted in excess of the 1:1 composition, the extraction increasing from strong to weak acids. It was therefore of interest to study whether a relatively strong acid like trichloroacetic acid ( $\text{p}K_{\text{HA}} = 0.64$ )<sup>9</sup> forms any polynuclear complexes. This acid is known to be fairly well extracted by organic solvents, but the data found in the literature describing its extraction are very inconsistent.

## EXPERIMENTAL

*Chemicals and solutions.* Trilaurylamine (Rhône-Poulenc) and *o*-xylene were the same as used in previous publications.<sup>1-7</sup> Trichloroacetic acid (HA) Merck, *p.a.* was used without further purification. Trichloroacetic acid and its salts decompose rapidly in aqueous solutions.<sup>10</sup> Hence it was not possible to store solutions of pure trichloroacetate salts. Before every titration a fresh solution of sodium trichloroacetate of pH  $\sim 5$  was prepared by neutralization of trichloroacetic acid with carbonate-free sodium hydroxide in a nitrogen atmosphere. This solution was standardized by determining sodium as sodium sulfate and then used for the preparation of 1.0 M NaA and 0.1 M HA + 0.9 M NaA. The acid solutions were standardized against  $\text{Ti}_2\text{CO}_3$  or standard 0.1 M NaOH. The residual acidity in 1.0 M NaA (of the order of 0.001 M) was determined from the first part of the  $E_0$  titration curve with the use of a Gran diagram.<sup>11</sup> The 0.1 M NaOH + 0.9 M NaA solution was prepared and standardized in a similar way.

The technique used in the emf work is described in detail elsewhere<sup>3</sup> except that in the present work the analytical concentration of HA, *i.e.*  $C_{\text{HA}} = [\text{H}^+]_{\text{aq}} + [\text{HA}]_{\text{aq}}$  was evaluated instead of  $[\text{H}^+]_{\text{aq}}$ . It was found that a plot of  $E - 59.16 \log C_{\text{HA}}$  was a linear function of  $C_{\text{HA}}$ . This behavior can be expected if the activity coefficients are kept constant by the ionic medium and the total anion concentration is kept practically constant as was done in the present study. This can be seen in the following way. For the dissociation of HA we have



$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a \frac{y(\text{HA})}{y(\text{H}^+)y(\text{A}^-)} \quad (2)$$

where  $y(\text{HA})$ ,  $y(\text{H}^+)$  *etc.* are the molar activity coefficients of HA,  $\text{H}^+$  *etc.* Here, as in the following, species and concentrations in the organic phase are given the subscript "org" and those in the aqueous phase are without subscript.

From the material balance for HA we have

$$C_{\text{HA}} = [\text{H}^+] + [\text{HA}] \quad (3)$$

$$C_{\text{HA}} = [\text{H}^+] \left( 1 + \frac{[\text{A}^-] y(\text{H}^+) y(\text{A}^-)}{K_a y(\text{HA})} \right) \quad (4)$$

From (4) is evident that proportionality exists between  $C_{\text{HA}}$  and  $[\text{H}^+]$  if activity coefficients and  $[\text{A}^-]$  are kept constant.

The  $E_0$ -values in the calibration titrations before and after every two-phase titration usually differed by a few tenths of a mV. For the calculation of  $C_{\text{HA}}$  for all points in the titration the average value of these two  $E_0$ -values was used.

The technique used in the batch experiments is described elsewhere.<sup>1</sup>

The two-phase titrations were carried out in an oil thermostat at  $25 \pm 0.02^\circ\text{C}$ , the batch experiments in a thermostated room at  $25 \pm 0.2^\circ\text{C}$ .

*Activities of trichloroacetic acid in aqueous solutions.* The activities in the system  $\text{CCl}_3\text{COOH}-\text{H}_2\text{O}$  were calculated from freezing point data found in the literature. The data of Pickering<sup>12</sup> cover the whole range of concentrations needed, but differ somewhat from the more accurate data of Drucker<sup>13</sup>

and Kendall and King,<sup>14</sup> which cover only part of the concentration range. We have ascribed this difference to a systematical error in the concentrations given by Pickering and corrected them accordingly.

Activity coefficients were calculated according to the usual method (*e.g.* Ref. 15):

$$-\log \gamma_{\pm} = 0.4343 j + 0.8686 \int_0^{\sqrt{m}} \frac{j}{\sqrt{m}} d\sqrt{m} - \xi \int_0^{\theta} \frac{\theta d\theta}{vm} \quad (5)$$

$$\text{where } j = 1 - (\theta/vm\lambda) \quad (6)$$

The symbols in eqns. (5) and (6) have their usual meaning.<sup>15</sup> The extrapolation of  $j/\sqrt{m}$  to  $\sqrt{m} = 0$  was made using the expressions of the interionic attraction theory, with a value of 4 Å for the mean distance of closest approach.<sup>16, p. 294</sup> The values of  $\gamma_{\pm}$  obtained at the freezing point temperature were transformed to 25°C by means of the relative partial molal heat content calculated from the heat of dissolution<sup>17</sup> and the relative partial molal heat capacity, determined from the limiting law,<sup>16, p. 124</sup> and then changed to the molarity scale, using the densities given by Drucker.<sup>13</sup> From the same data<sup>12-14</sup> the values of the water activity in solutions of trichloroacetic acid were computed. The values of the activity coefficients of the trichloroacetic acid and the activity of water are given in Table 1.

Table 1. The mean activity coefficients of trichloroacetic acid and the activity of water in its aqueous solutions at 25°C calculated from data given by Pickering,<sup>12</sup> Drucker,<sup>13</sup> and Kendall and King.<sup>14</sup>

$C_{\text{CCl}_3\text{COOH}}$	$\{\text{H}_2\text{O}\}$	$\gamma_{\pm}(\text{CCl}_3\text{COOH})$
0.2	0.922	0.749
0.4	0.985	0.704
0.6	0.978	0.686
0.8	0.971	0.679
1.0	0.964	0.672
1.5	0.948	0.644
2.0	0.932	0.612
2.5	0.920	0.565
3.0	0.909	0.519
3.5	0.899	0.475
4.0	0.890	0.440
4.5	0.881	0.412
5.0	0.874	0.391

The activity coefficients calculated in this paper differ considerably from those reported by Brown and Mathieson.<sup>18</sup> This difference is caused mainly by differences in the formalism used for the evaluation of the activity coefficients. The activity coefficients obtained in our calculations are (stoichiometric) mean ionic activity coefficients  $\gamma_{\pm}$ , defined by

$$\{\text{H}^+\} \{\text{CCl}_3\text{COO}^-\} = C_{\text{HA}}^2 \gamma_{\pm}^2 \quad (7)$$

Brown and Mathieson have introduced the (quite uncertain) degree of dissociation  $\alpha$  in evaluating the activities from freezing points. In their equilib-

rium eqn. (3) they use  $cf$  for the activity of monomer HA in the aqueous phase. It is not clear to us from their eqns. (4) and (5) what their "f" really signifies.

### The distribution of trichloroacetic acid between water and *o*-xylene

The distribution of trichloroacetic acid and water between water-acid mixtures and *o*-xylene is shown in Fig. 1 where  $C_{\text{HA,org}}$  and  $C_{\text{H}_2\text{O,org}}$  are plotted against  $C_{\text{HA}}$ .  $C_{\text{H}_2\text{O,org}}$  has been corrected for the water extracted by the diluent itself, corrections being calculated per weight of diluent. (It has been found that a simple distribution equilibrium describes the water extraction by *o*-xylene,<sup>19</sup>  $\text{H}_2\text{O}_{\text{aq}} \rightleftharpoons \text{H}_2\text{O}_{\text{org}}$ ,  $k = 0.021$ ). After correcting for volume changes the material balance held within a few per cent for most of the points. The primary experimental data are given in Table 2.

Table 2. The corresponding values of  $C_{\text{HA}}$ ,  $C_{\text{HA,org}}$ , and  $C_{\text{H}_2\text{O,org}}$  for the distribution of trichloroacetic acid and water between water-acid mixtures and *o*-xylene.

0.362, 0.0136, 0.0342; 0.519, 0.0260, 0.0475; 0.758, 0.0570, 0.0752; 1.201, 0.141, 0.163; 1.787, 0.306, 0.0334; 2.485, 0.495, 0.559; 2.525, 0.487, 0.552; 2.930, 0.632, 0.728; 3.404, 0.728, 0.881; 4.113, 0.897, 1.185.

In Fig. 2 the dependence of  $\log C_{\text{HA,org}}$  on the logarithm of the activity of HA in the aqueous phase is shown. The slope of the curve is unity at lower concentrations of HA, but increases with increasing concentration. The simplest explanation is that part of HA in the organic phase is dimerised. There is spectroscopic evidence of dimerisation of HA in nonpolar organic solvents.<sup>20</sup>

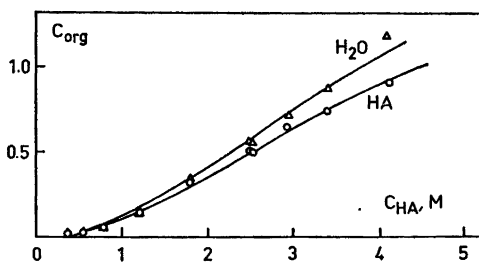


Fig. 1. The concentrations of trichloroacetic acid (O) and water ( $\Delta$ ) extracted into *o*-xylene as a function of the concentration of the acid in the aqueous phase.

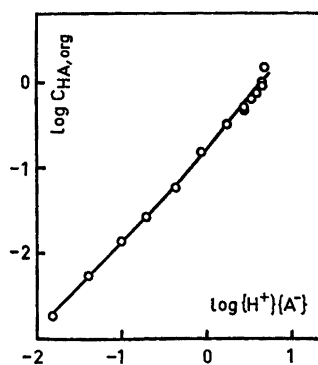
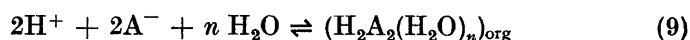
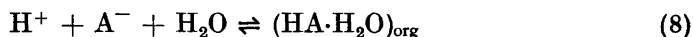


Fig. 2. The extraction of trichloroacetic acid in *o*-xylene as a function of the activity of trichloroacetic acid in the aqueous phase.

From a comparison of the curves in Fig. 1 it follows that, in the range where the monomer predominates,  $C_{\text{HA,org}}$  is nearly equal to  $C_{\text{H}_2\text{O,org}}$  and hence the monomer seems to be monohydrated. With increasing concentration of HA in the organic phase, the difference between  $C_{\text{H}_2\text{O,org}}$  and  $C_{\text{HA,org}}$  increases also, suggesting that the dimer is hydrated by more than two molecules of water per dimer. We assume the species present are  $\text{HA}\cdot\text{H}_2\text{O}$  and  $\text{H}_2\text{A}_2(\text{H}_2\text{O})_n$



The equilibrium constants for these reactions are

$$k_{1,1} = [\text{HA}\cdot\text{H}_2\text{O}]_{\text{org}} \{\text{H}^+\}^{-1} \{\text{A}^-\}^{-1} \{\text{H}_2\text{O}\}^{-1} \quad (10)$$

$$k_{2,n} = [\text{H}_2\text{A}_2(\text{H}_2\text{O})_n]_{\text{org}} \{\text{H}^+\}^{-2} \{\text{A}^-\}^{-2} \{\text{H}_2\text{O}\}^{-n} \quad (11)$$

and in the organic phase the following material balances hold

$$C_{\text{H}_2\text{O,org}} = k_{1,1} \{\text{H}^+\} \{\text{A}^-\} \{\text{H}_2\text{O}\} + nk_{2,n} \{\text{H}^+\}^2 \{\text{A}^-\}^2 \{\text{H}_2\text{O}\}^n \quad (12)$$

$$C_{\text{HA,org}} = k_{1,1} \{\text{H}^+\} \{\text{A}^-\} \{\text{H}_2\text{O}\} + 2k_{2,n} \{\text{H}^+\}^2 \{\text{A}^-\}^2 \{\text{H}_2\text{O}\}^n \quad (13)$$

The value of  $n$  has been found by plotting  $C_{\text{H}_2\text{O,org}} \{\text{H}^+\}^{-1} \{\text{A}^-\}^{-1} \{\text{H}_2\text{O}\}^{-1}$  against  $n \{\text{H}^+\} \{\text{A}^-\} \{\text{H}_2\text{O}\}^{n-1}$  and on the same scale  $C_{\text{HA,org}} \{\text{H}^+\}^{-1} \{\text{A}^-\}^{-1} \{\text{H}_2\text{O}\}^{-1}$  against  $2 \{\text{H}^+\} \{\text{A}^-\} \{\text{H}_2\text{O}\}^{n-1}$  for  $n = 2, 3$ , or  $4$  (Fig. 3). The best fit has been found for  $n = 3$  and the values of the equilibrium constants calculated:  $k_{1,1} = (2.0 \pm 0.2) \times 10^{-1}$ ,  $k_{2,3} = (2.3 \pm 0.2) \times 10^{-2}$ . By using  $k_{1,1}$  and  $k_{2,3}$ , the dimerisation constant, as usually defined as

$$k_2 = [\text{H}_2\text{A}_2][\text{HA}]^{-2} \quad (14)$$

was calculated as

$$k_2 = (0.57 \pm 0.05) \{\text{H}_2\text{O}\}$$

The dimerisation of trichloroacetic acid has been studied by many investigators, but the values for the dimerisation constant found differ by

Table 3. Dimerisation constants of trichloroacetic acid in nonpolar organic solvents.

Solvent	Dimerisation constant	Method of determination	Ref.
Benzene	6.5	heat of dimerisation	23
	7.0	cryoscopy	24
	2.20	IR-spectra	21
Toluene	6.0	distribution	23
	3.0	heat of dimerisation	23
	5.0	distribution	23
<i>m</i> -Xylene	555	distribution	18
	1.0	heat of dimerisation	23
<i>o</i> -Xylene	$(0.57 \pm 0.05) \{\text{H}_2\text{O}\}$	distribution	this work
Carbon tetrachloride	1060	IR-spectra	22
Chloroform	833	distribution	18

about 3 powers of ten. In Table 3 the most reliable data are summarized. They can be divided into two categories according to the definition of the distribution and dimerisation constants and the methods of measurement.

1. Measurements in dry organic solvents. To this category belong the IR-spectrometry measurements<sup>21,22</sup> (where it is stated that the solutions were dried) and probably the calorimetric<sup>23</sup> and cryoscopic data.<sup>24</sup> These sets of data are very inconsistent and this can hardly be ascribed to differences in solvents only. In dry solutions higher dimerisation constants can be expected than in solvents equilibrated with water, because in solutions saturated with water there is competition between dimerisation and hydration of the monomer. Bell and Arnold<sup>25</sup> have made a cryoscopic study of HA in benzene solutions. They have found that, in dry solutions up to the 0.1 m, the dimer is the prevailing species, but in wet solutions the only important species is the monohydrated monomer.

2. Measurements in two-phase systems. The only comparable data in the literature are those of Brown and Mathieson.<sup>18</sup> Calvet and Paoli<sup>23</sup> mentioned unpublished results of Guillerm, but since we do not know the experi-

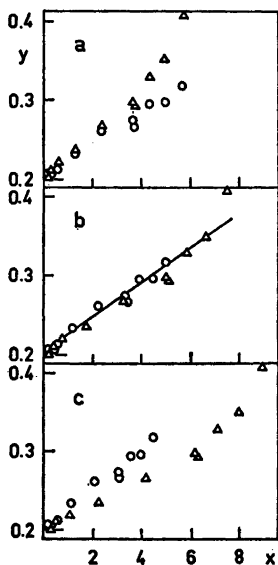


Fig. 3. Graphical calculation of the equilibrium constants of the complexes  $\text{HA}\cdot\text{H}_2\text{O}$  and  $\text{H}_2\text{A}_2\cdot(\text{H}_2\text{O})_n$ . The coordinates are:

$$\circ x: 2\{\text{H}^+\}\{\text{A}^-\}\{\text{H}_2\text{O}\}^{n-1}$$

$$y: C_{\text{HA,org}}\{\text{H}^+\}^{-1}\{\text{A}^-\}^{-1}\{\text{H}_2\text{O}\}^{-1}$$

$$\Delta x: n\{\text{H}^+\}\{\text{A}^-\}\{\text{H}_2\text{O}\}^{n-1}$$

$$y: C_{\text{H}_2\text{A}_2,\text{org}}\{\text{H}^+\}^{-1}\{\text{A}^-\}^{-1}\{\text{H}_2\text{O}\}^{-1}$$

$n = 2$  (Fig. 3a),  $n = 3$  (Fig. 3b),  $n = 4$  (Fig. 3c).

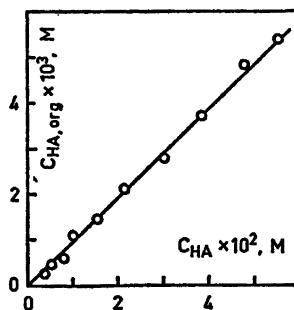


Fig. 4. Distribution of trichloroacetic acid between *o*-xylene and 1 M  $(\text{H,Na})\text{A}$  solutions.

mental details and the method of computation it is difficult to compare his results with ours. The main difference between Brown and Mathieson's results<sup>18</sup> and ours lies in the estimation of the activities of HA in the aqueous phase, as was discussed earlier.

THE SYSTEM TLA-*o*-XYLENE-H<sub>2</sub>O

Two-phase titration study of the distribution of trichloroacetic acid

This investigation has been carried out for three concentrations of TLA in *o*-xylene (1 %, 4 %, and 10 %) and aqueous phase of constant ionic strength 1.00 M (Na,H)A.

From two-phase titration emf data without TLA in the organic phase, (Fig. 4) the distribution constant of trichloroacetic acid monomer was obtained as

$$k_D = [\text{HA}]_{\text{org}}/C_{\text{HA}} = 0.097 \pm 0.010 \quad (15)$$

This result indicates that the activity coefficient of HA in the organic phase is constant over the range of acidities studied ( $5 \times 10^{-3}$ – $5 \times 10^{-2}$  M), in agreement with eqn. (4) and with the linear dependence of ( $E - 59.16 \log C_{\text{HA}}$ ) on  $C_{\text{HA}}$ .

Table 4. Corresponding values of  $-\log C_{\text{HA}}$ ,  $Z_{\text{HA}}$  obtained by two-phase titration.

0.0154 M TLA: 7.0511, 0.442; 6.4858, 0.764; 5.2552, 1.028; 3.2437, 1.212; 2.8685, 1.361; 2.6369, 1.481; 2.4713, 1.579; 2.2380, 1.714; 2.0791, 1.798; 1.9608, 1.847; 1.8746, 1.904; 1.7698, 1.937;
0.0610 M TLA: 7.3394, 0.264; 7.0707, 0.410; 6.6802, 0.663; 6.0953, 0.914; 3.3773, 1.138; 2.7738, 1.342; 2.5744, 1.437; 2.3783, 1.588; 2.1433, 1.734; 1.9405, 1.828; 1.8137, 1.889.
0.0630 M TLA: 7.7705, 0.096; 7.4222, 0.216; 6.9861, 0.456; 6.6362, 0.695; 5.9855, 0.934; 3.6799, 1.085; 3.3114, 1.154; 3.0916, 1.221; 2.7907, 1.347; 2.5761, 1.461; 2.3952, 1.558; 2.1856, 1.675; 1.9320, 1.793; 1.7512, 1.855;
0.0609 M TLA (back titration): 7.0047, 0.401; 6.5991, 0.664; 6.2424, 0.840; 6.1072, 0.884; 5.9060, 0.927; 5.7573, 0.949; 5.5646, 0.971; 4.6078, 1.014; 3.9976, 1.032; 3.7525, 1.050; 3.4787, 1.089; 3.1677, 1.160; 2.9706, 1.230; 2.6888, 1.363; 2.4748, 1.484; 2.2924, 1.591; 2.1332, 1.683; 1.9954, 1.764; 1.8722, 1.833;
0.155 M TLA: 3.4702, 1.137; 3.0409, 1.248; 2.7857, 1.350; 2.5135, 1.4916; 2.1839, 1.669; 1.9540, 1.776; 1.7918, 1.837;
0.161 M TLA: 7.7539, 0.124; 7.4107, 0.249; 6.9561, 0.500; 6.4473, 0.751; 6.2360, 0.875; 5.9993, 0.938; 5.3908, 1.000; 4.4020, 1.030; 3.8746, 1.059; 3.6109, 1.086; 3.4402, 1.114; 3.0399, 1.222; 2.6932, 1.372; 2.3220, 1.581; 2.0157, 1.743; 1.8161, 1.837.

The experimental data for the extraction with TLA were corrected for the extraction of HA by *o*-xylene, and the number of acid molecules per TLA,  $Z_{\text{HA}} = [\text{HA}]_{\text{org}}/[\text{TLA}]_{\text{tot}}$ , was then computed. The data are given in Table 4. In Fig. 5  $Z_{\text{HA}}$  is plotted against  $\log C_{\text{HA}}$  for the three concentrations of TLA studied together with data for a back titration at 4 % TLA with

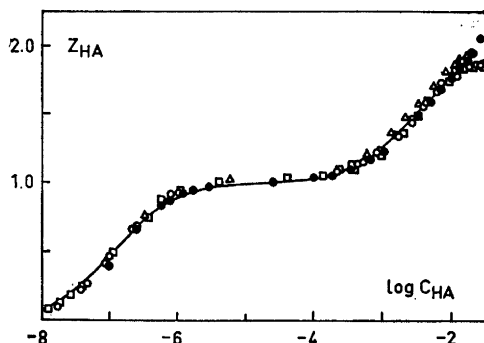


Fig. 5.  $Z_{\text{HA}}$  obtained by the two-phase emf-titrations in the system 1 M (H,Na)A—TLA-*o*-xylene.  $\Delta$  1 % TLA,  $\circ$  4 % TLA,  $\bullet$  4 % TLA back titration,  $\square$  10 % TLA. The curve was calculated with  $\log k_{1,1} = 6.93$ ,  $\log k_{1,2} = 9.44$ .

0.1 M NaOH. (Since the back titration was performed with 0.1 M NaOH + 0.9 M NaA solution, the ionic strength was not constant in this set of measurements, but was varied in the range 1.0—0.94.) It can be seen that, although HA and NaA decompose in aqueous solutions,<sup>10</sup> the back and forward titrations coincide, indicating that equilibrium is established. The experimental points seem to fall on a single curve until  $\log C_{\text{HA}} = -2$ . Beyond that point a considerable spread was obtained and therefore the calculations have been performed only on the range  $\log C_{\text{HA}} < -2$ .

Since the data for the three concentrations fall on a single curve and since the base form is known to be non-aggregated in aromatic hydrocarbons<sup>26</sup> the species must be mononuclear. The data could be explained by assuming two complexes TLA(HA) and TLA(HA)<sub>2</sub>. No conclusions about mixed acid-water complexes can be drawn from the emf titrations only, because the water in the organic phase was not determined. There is no evidence of polynuclear complexes as has been found with the strong mineral acids. Approximate values for the equilibrium constants

$$k_{p,q} = [(\text{TLA})_p(\text{HA})_q]_{\text{org}}[\text{TLA}]_{\text{org}}^{-p}C_{\text{HA}}^{-q} \quad (16)$$

were calculated by the Rossotti and Rossotti<sup>27</sup> extrapolation method and refined with the Algol version of the computer program LETAGROPVRID.<sup>28</sup> The final values for these constants are (the limits correspond to  $3\sigma$  ( $k$ )):

$$\log k_{1,1} = 6.93 \pm 0.03 \quad \log k_{1,2} = 9.44 \pm 0.04$$

The curve in Fig. 5 has been computed with the aid of these two constants.

#### Distribution of trichloroacetic acid for high concentrations of HA

The distribution of HA and the extraction of water has been determined by batch experiments for the following concentrations:

$$\begin{aligned} [\text{TLA}]_{\text{tot}} &= 0.111 \text{ M (5.80 \%)} \text{ and } 0.365 \text{ M (19.05 \%)} \\ [\text{HA}]_{\text{tot}} &= 0.1\text{--}6.5 \text{ M} \end{aligned}$$



In order to obtain  $Z_{\text{HA}}$  and  $Z_{\text{H}_2\text{O}} = [\text{H}_2\text{O}]_{\text{TLA}}/[\text{TLA}]_{\text{tot}}$ , the amount of acid and water extracted have been corrected for the extraction of acid or water by *o*-xylene and for the volume changes. The data are given in Table 5.

Table 5. Corresponding values of  $\{\text{H}^+\}\{\text{A}^-\}$ ,  $\{\text{H}_2\text{O}\}$ ,  $Z_{\text{HA}}$  and  $Z_{\text{H}_2\text{O}}$  obtained by batch extraction experiments.

0.111 M TLA: 0.00493, 0.996, 1.663, 0.230; 0.0601, 0.987, 2.163, 0.365; 0.165, 0.979, 2.302, 0.408; 0.335, 0.970, 2.571, 0.552; 0.850, 0.950, 2.985, 0.974; 1.365, 0.936, 3.246, 1.403; 1.875, 0.923, 3.815, 1.817; 2.073, 0.916, 3.766, 1.929; 2.285, 0.912, 3.870, 1.852; 2.692, 0.902, 4.045, 2.672; 2.950, 0.894, 4.168, 3.131; 2.994, 0.893, 4.491, 3.900;

0.365 M TLA: 0.0326, 0.991, 1.948, 0.252; 0.0838, 0.985, 2.276, 0.290; 0.554, 0.960, 2.709, 0.647; 0.800, 0.952, 3.227, 0.959; 1.360, 0.936, 3.569, 1.460; 1.954, 0.921, 3.600, 1.398; 2.478, 0.907, 3.966, 2.449; 2.534, 0.906, 3.921, 2.509; 2.806, 0.898, 4.193, 3.237; 2.954, 0.894, 5.060, 4.495; 3.170, 0.888, 5.429, 5.956.

The amount of HA and water extracted was computed by means of the previously determined equilibrium constants for the hydrated monomer and dimer and the actual volume of the organic phase at equilibrium, together with the amount of water extracted by *o*-xylene itself.<sup>19</sup>

The solubility of TLA in the aqueous phase is reported to be negligible for nitric and hydrochloric acid media and hence its solubility was neglected for this system. The corrected values of  $C_{\text{HA,TLA}}$  and  $[\text{H}_2\text{O}]_{\text{TLA}}$  were then used for calculation of  $Z_{\text{HA}}$  and  $Z_{\text{H}_2\text{O}}$  (Fig. 6).

As the values of  $Z_{\text{HA}}$  or  $Z_{\text{H}_2\text{O}}$  fall on the same curve for both concentrations of TLA, mononuclear complexes of the general formula  $\text{TLA}(\text{HA})_p(\text{H}_2\text{O})_q$  are formed. The concentration of the base form of TLA is very low and we

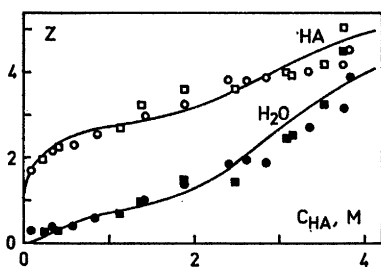


Fig. 6.  $Z_{\text{HA}}$  (open symbols) and  $Z_{\text{H}_2\text{O}}$  (full symbols) as a function of the concentration of trichloroacetic acid in the aqueous phase. Organic phase: 0.111 M TLA ( $\circ$ ,  $\bullet$ ) 0.365 M TLA ( $\square$ ,  $\blacksquare$ ) in *o*-xylene. The solid curves were calculated with  $\log k_{1,0} = 7.22$ ,  $\log k_{2,0} = 10.00$ ,  $\log k_{3,1} = 10.8$  and  $\log k_{7,7} = 9.19$ .

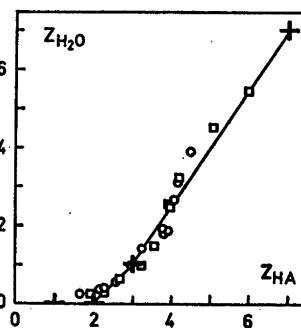


Fig. 7.  $Z_{\text{H}_2\text{O}}$  as a function of  $Z_{\text{HA}}$  for the extraction of trichloroacetic acid by 0.111 M TLA ( $\circ$ ) and 0.365 M TLA ( $\square$ ) in *o*-xylene.

can therefore put  $Z_{\text{HA}} \approx \bar{p}$ ,  $Z_{\text{H}_2\text{O}} \approx \bar{q}$ , where the average values of  $\bar{p}$  and  $\bar{q}$  are defined as

$$\bar{p} = \frac{\sum p c_{pq}}{\sum c_{pq}} \quad \text{and} \quad \bar{q} = \frac{\sum q c_{pq}}{\sum c_{pq}} \quad (17), (18)$$

$c_{pq}$  being the concentration of the complex  $\text{TLA}(\text{HA})_p(\text{H}_2\text{O})_q$  (*cf.* Sillén<sup>29</sup>).

From the plot  $\bar{q} = f(\bar{p})$  (Fig. 7) preliminary conclusions on the composition of particular complexes could be drawn. The first two complexes  $\text{TLA}(\text{HA})$  and  $\text{TLA}(\text{HA})_2$  (found in the two-phase titration experiments also) do not seem to contain any bound water molecules. For the high  $C_{\text{HA}}$  there is considerable spread in the data, caused mainly by the large volume changes and by the large amount of trichloroacetic acid extracted by *o*-xylene itself, making the amount extracted by the amine sometimes a rather small difference (*e.g.* the amount of HA extracted by the diluent component of the 0.111 M TLA and 0.365 M TLA solutions in equilibrium with aqueous 2 M HA is 49 % and 23 %, respectively). Hence the composition of higher complexes can be established from the  $\bar{p}$  vs.  $\bar{q}$  diagram only approximately. By means of the computer program LETAGROPVRID<sup>28</sup> we estimated equilibrium constants

$$k_{p,q} = [\text{TLA}(\text{HA})_p(\text{H}_2\text{O})_q][\text{TLA}]^{-1}\{\text{H}^+\}^{-p}\{\text{A}^-\}^{-p}\{\text{H}_2\text{O}\}^{-q} \quad (19)$$

for various complexes, error square sums ( $U$ ) of measured and computed  $Z_{\text{HA}}/Z_{\text{H}_2\text{O}}$  values and standard deviations ( $\sigma(y)$ ) in  $Z_{\text{HA}}/Z_{\text{H}_2\text{O}}$ .

Complexes with the following combinations of  $(p,q)$  were tried: (1,0), (2,0), (3,1), (4,2), (5,5), (5,6), (5,7), (5,8), (5,9), (6,6), (6,7), (6,8), (6,9), (7,7), (7,8), (7,9), and (8,9).

For  $k_{1,0}$  and  $k_{2,0}$ , the values found from the two-phase titration after correction for the activity of HA have been used. The activity factors of  $\text{H}^+\text{A}^-$  in the solution with NaA has been computed by means of Harned's rule; for the activity factors of NaA those of sodium acetate<sup>15</sup> were used.

The lowest  $U$  and lowest deviations in equilibrium constants have been found for the following "best" set:

$$\begin{aligned} \log k_{1,0} &= 7.22, \log k_{2,0} = 10.00, \log k_{3,1} = 10.8 \pm 0.3, \\ \log k_{7,7} &= 9.19 \pm 0.03, U = 0.186, \sigma(y) = 0.094. \end{aligned}$$

The curves in Fig. 6 are calculated with these constants. From the comparison of the above mentioned "best" set of complexes with other sets with rather low  $U$ -values *e.g.* for (1,0), (2,0), (3,1), (6,6)  $U = 0.234$ ,  $\sigma(y) = 0.106$ ; for (1,0), (2,0), (3,1), (5,6), (6,6)  $U = 0.237$ ,  $\sigma(y) = 0.109$ , it follows that complexes with  $(p,q)$  equal to (1,0), (2,0) and (3,1) are well established. For the higher complexes, taking into account the low accuracy of the experimental data in the region where they predominate, the rather small differences in the respective  $U$ -values cannot be taken as an unambiguous proof for the existence of one particular complex. For this reason the (7,7) complex should be taken only as a representative of higher complexes.

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