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Short Communications

On the Extraction with Long-chain Amines. XXVIII.
The System TLA – $CHCl_3$ – HCl and Aqueous 1.00 M LiCl at 25 °C

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In all solvents studied so far by the Stockholm group, the salts of trilaurylamine (= TLA) have been found to be associated.[1] In the hope of finding a nonaggregating system, it was decided to use chloroform as solvent. The experiments were performed as emf titrations[2] at 25.0 ± 0.05 °C, and chloroform and LiCl were purified as described elsewhere.[3,4] The amine concentrations used were: 7.9, 17.0, 17.6, 72.9 and 147.3 mM.

In Fig. 1 Z is plotted against lg h, where Z is defined by

$$Z = [\mathrm{HCl}]_{\mathrm{org}}/[\mathrm{TLA}]_{\mathrm{tot,org}} = H/B \qquad (1)$$

and $h = [\mathrm{H}^+]_{\mathrm{aq}}$, the hydrogen ion concentration as measured by a glass electrode calibrated in terms of hydrogen ion concentration.[2] Since $[\mathrm{Cl}^-]_{\mathrm{aq}} = 1.00$ the product $h[\mathrm{Cl}^-]$ is equal to h [*cf.* reaction (2)].

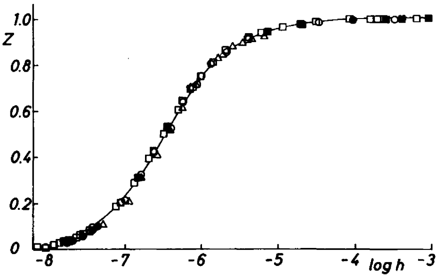

Fig. 1. Z plotted against lg h for: ○, 7.9 mM TLA; ●, 17.0 mM TLA; □, 17.6 mM TLA; ■, 72.9 mM TLA; △, 147.3 mM TLA. The curve has been computed from the eqn $Z = 10^{6.48}h(1 + 10^{6.48}h)^{-1}$.

In Fig. 1 practically all data fall on a single curve, with the exception of the highest amine concentration. However, the shift is in the wrong direction for association to occur and this must be due to some systematic error in the titration. It can thus be concluded that the association is practically negligible in chloroform. By using the well-known method of normalized curves[5] the equilibrium constant of the reaction

$$\mathrm{TLA(org)} + \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} \rightleftharpoons \mathrm{TLAHCl(org)} \qquad (2)$$

was found to be

$$\lg k_{1,1} = 6.48$$

Using the least-squares minimizing program LETAGROP[6] the following value was obtained

$$\lg k_{1,1} = 6.475 \pm 0.014$$

When taking systematic errors into account (a possible reason for the shift of the curve $Z(\lg h)$ for the highest amine concentration) the following value was obtained

$$\lg k_{1,1} = 6.510 \pm 0.015$$

Since we did not further investigate possible systematic errors we prefer to give

$$\lg k_{1,1} = 6.48 \pm 0.03 \qquad (3)$$

Table 1. VPO-data for TLA and TLAHCl at 25 °C. Concentrations in M (mol l^{-1}).

TLA B(M)	$\Delta R/B$ (ohm M^{-1})	TLAHCl B(M)	ΔR (ohm)	$\bar{n}$
0.0174	367	0.0135	5.02	0.998
0.0281	373	0.0242	8.93	1.005
0.0616	369	0.0465	17.11	1.008
0.0800	368	0.0717	26.89	0.989
0.1084	374	0.0990	36.33	1.010
0.1527	377	0.1500	59.10	0.942
Average:	371 ± 4		Average:	0.992 ± 0.026

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When comparing experimental and calculated Z-values all data with the exception of 3–4 experimental points fall within ± 0.02 in Z, which can be regarded as an acceptable fit. Anyone interested in the primary experimental data and the comparison of the calculated and experimental Z-values can write to Erik Högfeldt.

That TLAHCl is monomeric in chloroform receives further independent support from some vapor phase osmometry (VPO) data. The first two columns in Table 1 give the stoichiometric concentration (B) in mol l^{-1} of TLA in chloroform at 25 °C together with $\Delta R/B$. ΔR is the measured unbalance of the resistance bridge in the Mechrolab Vapor Phase Osmometer (model 301 A) used. Using the calibration constant obtained from these data the true concentration of TLAHCl (B') can be computed from the measured ΔR in solutions of TLAHCl in chloroform. That TLA is a suitable calibration substance is due to the fact that it is monomeric in organic solvents.[7] The average degree of association ($\bar{n}$) is now computed from B/B'. As seen from the last column in Table 1 all data cluster around $\bar{n}=1$, the average being 0.992 ± 0.026 and no association was found for TLAHCl in chloroform.

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