Extraction of Zinc Chloride by Trilaurylammonium Chloride and Trilaurylamine in Xylene
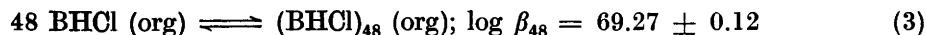
DAVID DYRSSEN and MARIA DE JESUS TAVARES*

Department of Analytical Chemistry,** University of Göteborg, Gibraltargatan 5 A,
Göteborg S, and Department of Inorganic Chemistry, Royal Institute of
Technology (KTH), Stockholm, 70, Sweden

Distribution experiments with ^{65}Zn have shown that the distribution ratio of Zn(II) between TLA·HCl (trilaurylammonium chloride) in o-xylene and HCl is proportional to $[\text{TLA·HCl}]^2_{\text{org,tot}}$ regardless of whether TLA·HCl is in the monomeric form or in an associated state. The distribution ratio between TLA (basic form) in o-xylene and 3 M LiCl is proportional to $[\text{TLA}]_{\text{org}}$. The distribution curves (log D vs. log [Cl$^-$]) for 0.5 % and 2 % TLA·HCl in o-xylene show a maximum for 3 M HCl or LiCl, indicating that the complex formation between Zn^{2+} and Cl$^-$ may be weaker than previous measurements have shown. Loading experiments with 2 % TLA·HCl and 3 M (H, Zn) Cl give additional proof that zinc(II) is present in the organic phase as ZnCl$_4^{2-}$.

AGGREGATION OF TRILAURYLAMMONIUM CHLORIDE IN o-XYLENE

Högfeldt and Tavares[1] have recently investigated the equilibria between trilaurylamine (TLA or B) in o-xylene and hydrochloric acid at 25°C for an aqueous phase with constant chloride concentration, i.e. 1 M (H,Li)Cl. From this study the following equilibria have been computed:[2]

$$\text{H}^+ \text{(aq)} + \text{Cl}^- \text{(aq)} + \text{B (org)} \rightleftharpoons \text{BHCl (org)}; \log K_a = 3.328 \pm 0.008 \quad (1)$$

$$3 \text{ BHCl (org)} \rightleftharpoons (\text{BHCl})_3 \text{ (org)}; \log \beta_3 = 3.096 \pm 0.024 \quad (2)$$

$$48 \text{ BHCl (org)} \rightleftharpoons (\text{BHCl})_{48} \text{ (org)}; \log \beta_{48} = 69.27 \pm 0.12 \quad (3)$$

Note that our $K_a = k_{1,1}$ and our $\beta_n = k_{n,n}/k_{1,1}{}^n$ as used in Refs. 1,2.

The organic phase should thus contain a monomer, a trimer and a rather large polymer, depending on the total concentration of BHCl in the o-xylene

---

* Present address: Laboratório de Física e Engenharia Nucleares, Sacavém, Portugal.
** Reprints and distribution data are available from this department.

Fig. 1. The concentration of TLA·HCl monomer as a function of the total concentration of TLA·HCl in *o*-xylene when $C_B = [BHCl]_{org} + 3\beta_3[BHCl]^3_{org} + 48\beta_{48}[BHCl]_{org}^{48}$. The dashed curve represents the case when the polymer $(BHCl)_{48}$ is neglected and the limiting value of log $[BHCl]_{org} = -1.42$ is set by the aggregation constant given by Högfeldt.[2]
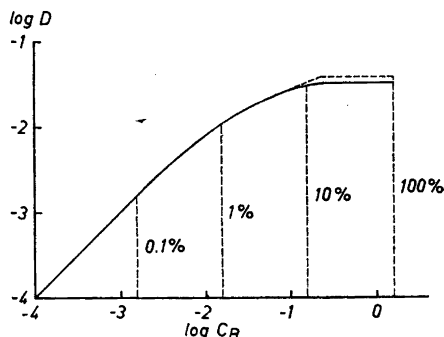
phase (C_B). Computer calculations have indicated a best fit with a polymer with $n = 48$ BHCl molecules, but other values of n are also in good agreement with the experimental data.

The values of β_3 and β_{48} are sufficient to calculate the concentration of the monomer, $[BHCl]_{org}$, as a function of the total concentration of BHCl in the organic phase

$$C_B = [BHCl]_{org} + 3\beta_3[BHCl]^3_{org} + 48\beta_{48}[BHCl]^{48}_{org} \qquad (4)$$

Fig. 1 shows that $C_B \approx [BHCl]_{org}$ at low C_B (> 0.1 %) and that log $[BHCl]_{org}$ approaches -1.48 at high C_B indicating that above log $C_B = -0.8$ (> 10 %) TLA·HCl behaves as a separate phase. In the presence of such a third phase the concentration of all species of BHCl in the diluent (*o*-xylene) should be constant.

In his treatment of the two-phase titration data [1] Högfeldt [2] has shown, that when large aggregates are formed, they can be treated as a separate phase with a constant product $[H^+][Cl^-][B]_{org} = 10^{-4.75}$, *i.e.* $[BHCl]_{org} = 10^{-4.75+3.33} = 10^{-1.42}$ using $K_a = 10^{3.33}$. The question then arises whether the polymer $(BHCl)_{48}$ belongs to the diluent or to the aggregated third phase. Fig. 1 also shows log $[BHCl]_{org}$ as a function of log $C_B = \log([BHCl]_{org} + 3\beta_3[BHCl]_{org})$ (dashed curve). The curve should show a discontinuity at log $[BHCl]_{org} = \sim1.42$ (16 % TLA·HCl) when the third phase is formed. Since no such discontinuity is discernible in two-phase titration experiments, a better fit with the experimental data is obtained by taking into account the presence of a higher polymer in between the monomer and trimer and the "point" of aggregation. The general experience is that the position of this "point" depends on stirring conditions, content of acid, water and metal salts, temperature *etc.*, and it is thus not always observed even if crystalline products do sometimes appear. Fig. 1 shows, however, that below 7 % TLA·HCl in *o*-xylene aggregation (third phase formation) can be neglected together with the formation of higher polymers such as $(BHCl)_{48}$.
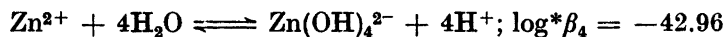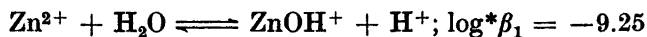
SCOPE OF INVESTIGATION AND SOME PREVIOUS WORK

The intention of this work was to use the recent information of the aggregation of a "liquid anion exchanger" in a distribution study of zinc(II). A similar distribution study of zinc(II) using 10 % methyldioctylammonium chloride in trichlorethylene has previously been carried out by Schindewolf.[3] Nothing is, however, known about the polymerization of R_3NHCl in this system, which restricts the treatment of the distribution data to some extent.

We also wished to make "loading" studies similar to those made on Dowex-1 by Horne, Holm and Meyers [4] to ascertain whether or not $ZnCl_4^{2-}$ is the dominant species in the organic phase at high concentrations of $ZnCl_2$. According to investigations of the complex formation between Zn^{2+} and Cl^- by Shchukarev, Lilich and Latysheva [5] as well as Short and Morris [6] and Biedermann [7] (who has obtained $K(ZnCl_3^- + Cl^- \rightleftharpoons ZnCl_4^{2-}) = 1.8$ in 5 M LiCl) the saturated complex in aqueous solutions is $ZnCl_4^{2-}$. The same conclusions as to the maximum ligand number have been confirmed by Raman studies [8] of $ZnCl_2$ and LiCl in methanol. Raman spectra [6] suggest a tetrahedral configuration of $ZnCl_4^{2-}$ in aqueous solutions and tributylphosphate extracts, but other Raman studies [10] indicate a planar structure. Furthermore, $ZnCl_4^{2-}$ seems to be a stable unit [11,12] with a tetrahedral configuration in several crystalline salts of the type M_2ZnCl_4. In addition there is also some evidence [9] that in aqueous solutions the Zn^{2+} ion coordinates, six molecules of water, and that the third complex is $ZnCl_3(H_2O)_2^-$ with a trigonal bipyramidal structure.

The distribution of zinc(II) between solid anion exchangers (e.g. Dowex-1) and chloride solutions has been studied by many workers. The most recent study has been published by Marcus and Maydan.[13] By correcting the distribution data for invasion in the resin of the electrolyte in the aqueous phase, they concluded that $ZnCl_4^{2-}$ was the main species in the anion exchange resin phase as well as the saturated species in the aqueous phase. No invasion of LiCl could be detected in the o-xylene-TLA·HCl phase (flame test for lithium; compare with Ref. 14). At HCl concentrations greater that 3 M HCl dissolves in the organic phase.[1]

Equilibrium (1) demonstrates that BHCl can be hydrolysed at low concentrations of HCl in the aqueous phase. As it has been shown [15,16] that $Cd(OH)_2$ and $Zn(OH)_2$ can be extracted by the basic form of Amberlite LA-1, the extraction of $ZnCl_2$ by R_3N in o-xylene from 3 M LiCl was also studied. The formation constants of $ZnOH^+$ and $Zn(OH)_4^{2-}$ in 3 M Na(Cl, OH) have been determined by Schorsch [17] to be as follows:

$$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+; \log^*\beta_1 = -9.25$$

$$Zn^{2+} + 4H_2O \rightleftharpoons Zn(OH)_4^{2-} + 4H^+; \log^*\beta_4 = -42.96$$

By the addition of small amounts of HCl to the 3 M LiCl phase we were able to keep the pH close to 6 and thus avoid the formation of $Zn(OH)_2$ as well as of BHCl.

EXPERIMENTAL

Reagents. The hydrochloric acid (Merck *p.a.*) was used without further purification. Lithium chloride (Mallinckrodt A.R. grade) was purified by double recrystallisation and

was then dissolved in doubly-distilled water. The dilute standard solutions were prepared from the concentrated stock solutions and were analysed for chloride by the Volhard volumetric method.

Zinc chloride (Merck p.a. $ZnCl_2$) was dried in an oven at 150°C and stored in a desiccator over silica gel.

Trilaurylamine, containing no more than 1 % N as primary and secondary amines, was supplied by Rhone-Poulenc and used without purification.

Analysis of the diluent, o-xylene (Fluka, reagent grade) by vapour phase chromatography showed the presence of 99 % o-xylene, 0.7 % m- and p-xylene and 0.07 % ethyl-benzene.

Freshly prepared amine solutions were used, which were stored in the dark to minimise decomposition when not in use.

Radioactive ^{65}Zn was supplied as an aqueous solution of zinc chloride by the Radiochemical Centre, Amersham, England. The concentration of Zn in this solution was 27.8 mg per 3.2 ml (0.133 M) and the total activity of ^{65}Zn was 10.1 mC. The radiochemical purity was checked by "double extraction" as follows: 1 % and 0.02 % TLA·HCl in o-xylene was shaken with ^{65}Zn in 3 M HCl. The organic layer was then shaken with inactive 3 M HCl. The measured log D values agreed to within 0.015 log units. The initial solution was diluted with either HCl or LiCl to solutions of known conentrations of HCl and LiCl, the final zinc concentration being either 0.0000133 M or 0.0000266 M. Practically no activity was lost in these experiments.

Distribution measurements. All the experiments were performed in a thermostated room at 25.0 ± 0.3°C.

In 50 ml glass stoppered tubes equal volumes (5 or 10 ml of each) of the organic and the aqueous phases were equilibrated by means of a mechanical Microid flask shaker (Griffin and Tatlock Ltd, England). It was found that agitation for 30 min with the Microid flask shaker was sufficient to attain equilibrium, whereas agitation by tilting the tubes with a mechanical rotator for 3 h was not, however, sufficient for the attainment of equilibrium. After equilibration the tubes were centrifuged and 4.00 ml aliquots of each phase were removed carefully, to avoid contamination of one phase by the other, by means of a pipette and transferred to 5 ml polyethylene counting tubes. These tubes were counted using a well-type, Tracerlab-SC-57 scintillation counter. The distribution ratio D for ^{65}Zn (organic/aqueous phase) was thus the ratio of the counts/min (corrected for background) in each phase.

The hydrochloric acid concentration in the initial aqueous phase of each sample was known. In some cases, however, where the concentration of the acid in the initial aqueous phase was less than 1 M after equilibration and centrifugation, aliquots of both phases were analysed for Cl^-.

In all the cases but the one represented in Fig. 4 the organic phase containing TLA was shaken four times with half of its volume of 1 M HCl in order to convert TLA to TLA·HCl before the metal extraction experiments. After agitation the two phases were allowed to settle in the dark. After phase separation, the organic solutions were filtered in order to remove possible suspended aqueous drops.

RESULTS AND DISCUSSION

D as a function of the concentration of BHCl. Two sets of data are shown in Fig. 2. The upper set represents experiments with 3 M HCl, the lower experiments with 0.5 M HCl. They fit fairly well to straight lines of gradient 2. At constant chloride concentration in the aqueous phase the ratios between the different chloride complexes of zinc(II) are constant, which can be seen from eqn. (7). The expression for D will then depend on how many BHCl react with $ZnCl_2$ according to eqns. (6) and (8).

$$D = \frac{[(BHCl)_m ZnCl_2]_{org}}{[Zn^{2+}] + [ZnCl^+] + [ZnCl_2] + [ZnCl_3^-] + [ZnCl_4^{2-}]} \tag{5}$$
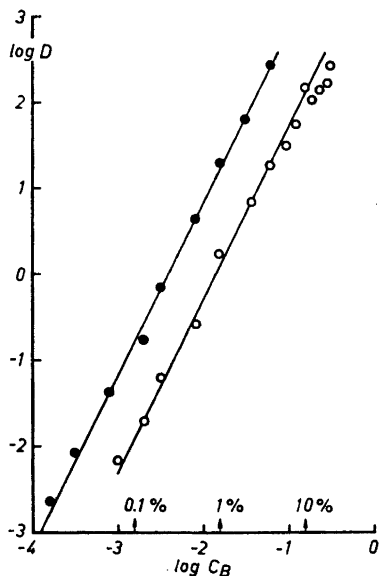
Fig. 2. Distribution of ⁶⁵Zn between o-xylene and HCl as a function of the total concentration of TLA·HCl in the organic phase. The open circles represent 0.5 M HCl and the filled circles 3 M HCl. The lines are drawn with a slope of 2.
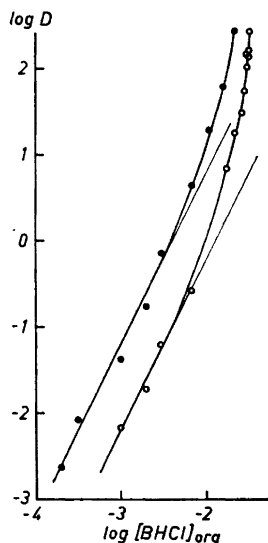
Fig. 3. Distribution of ⁶⁵Zn between solutions of TLA·HCl in o-xylene and 0.5 M HCl (open circles) or 3 M HCl (filled circles). The data are plotted as log D against log [BHCl]$_{\mathrm{org}}$, the conc. of the monomer of TLA·HCl in the organic phase. The straight part of the curves are drawn with a slope of 2.

or

$$D = \frac{K_m[\mathrm{BHCl}]_{\mathrm{org}}{}^m\beta_2[\mathrm{Cl}^-]^2}{1 + \beta_1[\mathrm{Cl}^-] + \beta_2[\mathrm{Cl}^-]^2 + \beta_3[\mathrm{Cl}^-]^3 + \beta_4[\mathrm{Cl}^-]^4} \tag{6}$$

where

$$[\mathrm{ZnCl}_n] = \beta_n[\mathrm{Zn}^{2+}][\mathrm{Cl}^-]^n \tag{7}$$

and

$$[(\mathrm{BHCl})_m\mathrm{ZnCl}_2]_{\mathrm{org}} = K_m[\mathrm{ZnCl}_2][\mathrm{BHCl}]_{\mathrm{org}}{}^m = K_m[\mathrm{BHCl}]_{\mathrm{org}}{}^m\beta_2[\mathrm{Zn}^{2+}][\mathrm{Cl}^-]^2 \tag{8}$$

Thus if log D is plotted against log [BHCl]$_{\mathrm{org}}$ at constant [Cl$^-$] the slope should give m. Fig. 3 shows that $m = 2$ at low concentrations of BHCl ($C_B \leq$ 0.004 M) where BHCl is mainly in the monomeric form. Fig. 3 and Fig. 1 also show that the slope of the curve log D vs. log [BHCl]$_{\mathrm{org}}$ increases when BHCl polymerises. The straight lines in Fig. 2 where log D is plotted against log C_B may imply that monomeric and polymeric BHCl react equally easily with ZnCl$_2$. The slope of 2 agrees very well with tendency of Zn^{2-} to form ZnCl$_4{}^{2-}$. The organic phase containing BHCl can be assumed to be a favorable medium for the formation of the saturated complex.

Even if slopes with small whole number gradient are very often obtained when log D for the distribution of a metal ion is plotted against the logarithm

of the total concentration of an alkylammonium salt, there are many exceptions, and the slope alone should not be taken as a proof of the formation of a certain metal complex. The number of BHX per MX_N can only be obtained if $\log D$ is plotted against $\log [BHX]_{org}$, the concentration of the monomeric form.

The value of K_2 can be determined from Fig. 3 using the values of β_n given in the literature. The values of $\beta_2[Cl^-]^2 (1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2 + \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4)^{-1}$ in 0.5 M HCl are as follows:

Shchukarev, Lilich and Latysheva:[5] 0.142
Short and Morris:[6] 0.169
Marcus and Maydan:[13] 0.261
Kivalo and Luoto:[18] 0.171

The mean value is $10^{-0.75}$ and from $\log D = \log K_2 + 2 \log [BHCl]_{org} - -0.73$ we obtain $\log K_2 = 4.53$, where K_2 represents the stability constant for the following equilibrium:

$$ZnCl_2 \text{ (0.5 M HCl)} + 2 \text{ BHCl } (o\text{-xylene}) \rightleftharpoons (BH)_2ZnCl_4 \text{ } (o\text{-xylene})$$
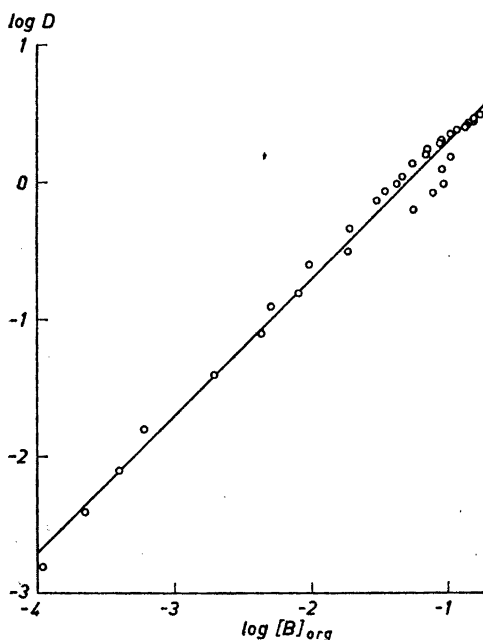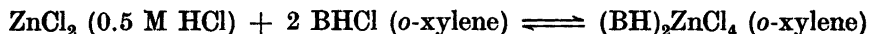

Fig. 4. Distribution of ^{65}Zn between solutions of TLA (base form) in o-xylene and 3 M LiCl. The data are plotted as $\log D$ against $\log [B]_{org}$. The straight line is drawn with a slope of 1.
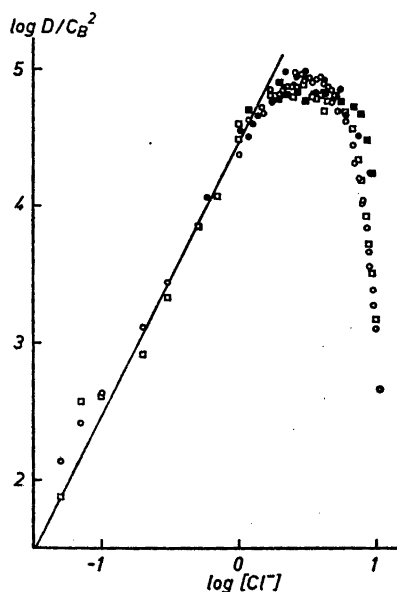
Fig. 5. Distribution of ^{65}Zn between TLA·HCl in o-xylene and HCl (open symbols) or LiCl (filled symbols). Squares represent 0.5 % TLA·HCl and circles represent 2 % TLA·HCl. The data are plotted as $\log D/C_B^2$ against $\log [Cl^-]$. The thin straight line is drawn with a slope of 2.

D as a function of the concentration of B. Fig. 4 shows that the distribution data for *o*-xylene-TLA and 3 M LiCl fit a straight line with a slope of 1 when plotted as log *D* vs. log $[B]_{org}$. As the two-phase titration data [1] showed that B has practically no tendency to associate with B or BHCl, which would probably not be the case with primary and secondary amines where hydrogen bonding can occur, we may explain the straight line by the following equilibrium (equilibrium constant *K*)

$$ZnCl_2 \ (3 \text{ M LiCl}) + B \ (o\text{-xylene}) \rightleftharpoons ZnBCl_2 \ (o\text{-xylene})$$

the expression for the net distribution ratio being

$$D = \frac{[ZnBCl_2]_{org}}{[Zn^{2+}] + [ZnCl^+] + [ZnCl_2] + [ZnCl_3^-] + [ZnCl_4^{2-}]} \qquad (9)$$

or

$$D = \frac{K[B]_{org}\beta_2[Cl^-]^2}{1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2 + \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4} \qquad (10)$$

As above we may use the values of β_n found by others in order to calculate $\beta_2[Cl^-]^2(1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2 + \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4)^{-1}$ for 3 M LiCl and then calculate *K*.

Shchukarev, Lilich and Latysheva:[5] 0.099
Short and Morris:[6] 0.150
Marcus and Maydan:[13] 0.136
Kivalo and Luoto:[18] 0.274

The mean of the first three values is $10^{-0.78}$ and from log *D* = log *K* + log $[B]_{org}$ −0.78 we obtain log *K* = 1.5.

One might have expected the formation of a complex with two B (ZnB_2Cl_2), but owing to steric hindrance it is unlikely that two molecules of such a large tertiary amine as TLA can be bound to $ZnCl_2$ to form a tetrahedral complex. Since we did not investigate the dependence on $[Cl^-]$, our experiments do not, however, rule out the possibility of the tetrahedral zinc complexes $Li^+ZnBCl_3^-$ and $ZnBCl_2.H_2O$.

D as a function of the concentration of Cl^-. Four sets of experiments were performed using two different concentrations of BHCl (0.5 and 2 %) and either HCl and LiCl in the aqueous phase in order to vary (Cl^-). The data are plotted as log D/C_B^2 (*cf.* Fig. 2) against log $[Cl^-]$ in Fig. 5. It may be seen from this figure that D/C_B^2 is practically the same for the two media up to *ca.* 6 M Cl^-. Above 6 M the distribution curve for LiCl lies above the curve for HCl; the same effect has also been observed by Schindewolf [3] in his investigation with 10 % methyldioctylammonium chloride in trichloroethylene.

It is tempting to explain the distribution curve by the expression for *D* given above (eqn. 6), as the first part of the distribution curve has a slope of 2 corresponding to

$$D = K_2[BHCl]^2_{org} \ \beta_2[Cl^-]^2 \qquad (11)$$

Furthermore, the distribution curve shows a maximum as can be predicted from eqn (6). In Fig. 6 we have tried to fit the distribution data in Fig. 5 to a
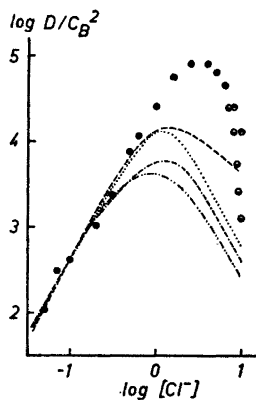
Fig. 6. Comparison between representative data from Fig. 5. and investigations of the complex formation between Zn^{2+} and Cl^- made by other authors. The shape of the distribution curve calculated from their data is fitted to the left part of the curve at lower $[Cl^-]$. Symbols: — — — Kivalo and Luoto,[18] .... Shchukarev, Lilich and Latysheva,[5] .—.—.—. Short and Morris,[6] —..—..— Marcus and Maydan.[13]
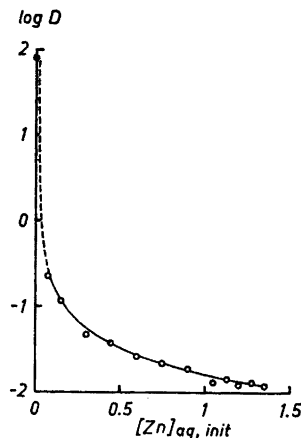
Fig. 7. Distribution of [65]Zn between 2 % (0.0312 M) TLA·HCl in *o*-xylene and 3 M (H, Zn)Cl as a function of the initial molar concentration of $ZnCl_2$ in the aqueous phase. The curve is calculated from $D = 0.0156/([Zn]_{aq,init} - 0.0156)$.

distribution curve whose form has been calculated (eqn. 6) using values of β_1, β_2, β_3, and β_4 found in the literature. None of the sets of constants given in Table 1 can, however, explain our distribution curve when fitted to the data for 0.1 M Cl^-. According to previous β_n values the distribution curve should have a maximum at $[Cl^-] \approx 1$ M and not at $[Cl^-] \approx 3$ M.

The maximum shifts to approximately 8 M if molar activities (1/2 log {LiCl} or 1/2 log {HCl}) instead of molar concentrations are plotted along the abscissa. So we are either dealing with a salting out effect or the complex formation between Zn^{2+} and Cl^- is considerably weaker than previous measurements have implied. The form of the curve calculated with the constants

Table 1. Stability constants β_n (eqn. 7) for the complex formation between Zn^{2+} and Cl^-.

Authors	Temp.	Ionic strength M	log β_1	log β_2	log β_3	log β_4
Shchukarev, Lilich and Latysheva [5]	25	4.5	−0.32	−0.05	−0.30	−0.15
Short and Morris [6]	20	0.7	0.72	0.49	−0.19	0.18
Marcus and Maydan [13]	25	0	0.43	0.61	0.53	0.20
Kivalo and Luoto [18]	25	2	−0.49	0.02	−0.07	

of Shchukarev, Lilich and Latysheva [5] would fit our distribution data up to $[Cl^-] \approx 6$ M if shifted 0.40 log $[Cl^-]$ units to the right. This means that their values of log β_n should be reduced by $n \times 0.40$.

Loading experiments. Fig. 7 shows how log D decreases when the zinc concentration is increased. At low zinc concentrations $(1.33 \times 10^{-5}$ M) $D \sim 80$ for 3 M HCl, so 98.8 % should be extracted at equal phase volumes. If Zn(II) is, however, extracted in the form of $ZnCl_4^{2-}$, then $[Zn]_{org,tot}$ cannot exceed 0.0156 M (half of the concentration of BHCl in the organic phase). If the organic phase containing BHCl is loaded at $[Zn]_{aq,init} > 0.0156$ M, then $D = 0.0156/([Zn]_{aq,init} -0.0156)$. A curve based on this equation is drawn in Fig. 7, and fits the experimental data extremely well. This furnishes an additional proof that Zn(II) is extracted as a tetrachloro-complex.

Note added in proof. Articles by Scibona, Orlandini, and Danesi [19] and by Lloyd [20] on amine extractions of zinc chloride have appeared during the publication of this work. We have compared their results with ours in a paper [21] read at the International Conference on Solvent Extraction Chemistry (ICSEC), which was has held in Göteborg, August 27 — September 1, 1966.

REFERENCES

1. Högfeldt, E. and de Jesus Tavares, M. *Trans. Roy. Inst. Technol. Stockholm*, (1964) No. 228.
2. Högfeldt, E. *Svensk Kem. Tidskr.* **76** (1965) 290.
3. Schindewolf, V. *Z. Elektrochem.* **62** (1958) 335.
4. Horne, R. A., Holm, R. H. and Meyers, M. D. *J. Phys. Chem.* **61** (1957) 1655.
5. Shchukarev, S. A., Lilich, L. S. and Latysheva, V. A. *Zh. Neorg. Khim.* **1** (1956) 225.
6. Short, E. L. and Morris, D. F. C. *J. Inorg. Nucl. Chem.* **18** (1961) 192.
7. Biedermann, G. *Private communication.*
8. Kecki, Z. *Spectrochim. Acta* **18** (1962) 1165.
9. Morris, D. F. C., Short, E. L. and Waters, D. N. *J. Inorg. Nucl. Chem.* **25** (1963) 975.
10. Irish, D. E., McCarroll, B. and Young, T. F. *J. Chem. Phys.* **39** (1963) 3436.
11. Morosin, B. and Lingafelter, E. C. *Acta Cryst.* **12** (1959) 611.
12. Brehler, B. *Z. Krist.* **114** (1960) 66; **109** (1957) 68.
13. Marcus, Y. and Maydan, D. *J. Phys. Chem.* **67** (1963) 979.
14. Scibona, G., Danesi, P. R., Orlandini, F. and Coryell, C. D. *J. Phys. Chem.* **70** (1966) 141.
15. Dyrssen, D. and Lumme, P. *Acta Chem. Scand.* **16** (1962) 1785.
16. Sekine, T. *Acta Chem. Scand.* **19** (1965) 1526.
17. Schorsch, G. *Thèses de l'université de Strasbourg* DE 280 (1964).
18. Kivalo, P. and Luoto, R. *Suomen Kemistilehti* **30 B** (1957) 163.
19. Scibona, G., Orlandini, F. and Danesi, P. R *J. Inorg. Nucl. Chem.* **18** (1966) 1313.
20. Lloyd, P. J. D. *Proc. ICSEC*, North-Holland 1967.
21. Dyrssen, D. and de Jesus Tavares, M. *Proc. ICSEC*, North-Holland 1967.

Received April 5, 1966.