# Extraction of HCl by Di-isononylamine Dissolved in Chloroform

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The equilibria involved in the extraction of HCl by a long-chain secondary aliphatic amine, di-isononylamine (DINA) (di(3,5,5-trimethylhexyl)amine) dissolved in chloroform, have been investigated by two-phase emf titrations, and, in the "excess acid" range, by simple batch experiments.

From data in the range $0 < Z_{HCl}$ (= HCl bound/total amine) < 1, and in the total amine concentration range, $0.006-0.30$ M, only one complex, the dimer $(DINAHCl)_2$, is found. The formation constant obtained for the reaction

$$2 \text{ DINA(org)} + 2\text{H}^+\text{(aq)} + 2\text{Cl}^-\text{(aq)} \rightleftharpoons (DINAHCl)_2\text{(org)}$$
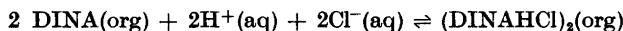
is: $\log (k_{22} \pm 3\sigma) = 15.479 \pm 0.014$

Water does not seem to play any important part in this reaction.

Extraction of excess HCl ($Z_{HCl} > 1$) occurs for $[\text{HCl(aq)}] \gtrsim 6$ M. It may be accounted for in terms of a mechanism of "statistical distribution" of HCl between ($Z_{max} - 1$) available sites per DINAHCl unit. The data do not suffice to distinguish among various models with $Z_{max} \geq 2$. Equilibrium constants are given for the two limiting cases

a) $Z_{max} = 2$ (eqns. (12a,b)), and
b) $Z_{max} \to \infty$ (eqns. (13)—(17)).

The extraction of water is low in this range also, and does not correspond to any simple stoichiometry.

The reactions and equilibria involved in extraction by long-chain alkyl ammonium salts have been studied extensively by many workers and many reviews have been published (Refs. 1—4 is a sampling). These ammonium salts are used in the atomic energy field for the separation and purification of actinides. They have also been used for analytical separations,[5] and for separating strong and weak acids.[6] Investigations of the mechanism by which the amine base form is converted to the corresponding salt are, however, quite rare. During the last few years, a group at this laboratory has used the technique of two-phase emf titration [7-9] to study the complex formation

occurring between long-chain tertiary amines (mainly trilaurylamine) and various acids. It is found (with strong acids) that complexes of the type $(HXB)_n$ (HX = acid; B = amine) are formed. The value of n is small (1−3) at low aqueous acidity ($= a = \{H^+\}\{X^-\}$) and low total amine concentration ($= B$). At higher values of a and B large aggregates seem to be formed ($n \sim 10$ to 50). No interaction (complex formation) between the free base form and the salt has been found. Ref. 2 is a review of the results up to 1964. A similar study with a different type of amine should be of interest.

This paper reports a study of the extraction of hydrochloric acid by a long-chain *secondary* aliphatic amine, di-isononylamine ("DINA", di(3,5,5-trimethyl-hexyl)-amine) dissolved in chloroform, employing two-phase emf titrations. In addition, simple batch experiments have been made to study the HCl (and H_2O) extraction in the range where all amine has been converted to the "salt". A few infrared spectroscopy experiments have also been performed in an attempt to obtain additional information.

EXPERIMENTAL

Chemicals and solutions

Di-isononylamine (di(3,5,5-trimethyl-hexyl)amine, $(C_9H_{19})_2NH$, DINA), was kindly supplied by the Imperial Chemicals Industries, Ltd., England, through the courtesy of Dr. K. M. Naprstek. It was reported by the supplier to be 99.1 % (w/w) pure (0.4 % H_2O). This was checked by:

a) vapor phase chromatography (VPC), which also indicated a purity of *ca.* 99 %;

b) determination of the equivalent weight of the hydrochloride by titration with standard alkali. The value obtained was 301 ± 3. (Theoretical: 306.0; the equivalent weight found is thus *ca.* 2 % low.)

The *chloroform* (Merck *p.a.*) used was washed 3−4 times with twice its volume of water to remove the 1 % ethanol in the commercial product. The purity of this chloroform was checked by VPC and found to be 99.8 % (H_2O 0.08 %). No ethanol was detectable (< 0.005 %). The VPC determinations were done by Mr. Gösta Lindgren of the Department of Analytical Chemistry, KTH.

The $CHCl_3$ used was also tested for HCl by $AgNO_3$.

Solutions of DINA in chloroform were prepared by pipetting DINA, weighing it in a calibrated volumetric flask and diluting, shortly before each experiment.

The *hydrochloric acid* (Merck *p.a.*) was used without further purification.

In order to keep the activity coefficients in the aqueous phase constant (in the two-phase emf titrations) the ionic medium 1.00 M (Li^+, H^+)Cl^- was used. *Lithium chloride* (Mallinckrodt A.R.) was re-crystallised once before use.

The following solutions were prepared:

1.000 M LiCl, 10 mM HCl + 990 mM LiCl, and 100 mM HCl + 900 mM LiCl*

The 100 mM HCl was standardized against Tl_2CO_3 (spectrographically pure). The solution containing 10 mM HCl was standardized against the 100 mM HCl solution by emf titration employing a graphical method outlined by Gran.[10] In the batch experiments various $HCl-H_2O$ mixtures were prepared, ranging from 0.3 to 11 M. The $Li^+(OH^-, Cl^-)$ solution used for back titrations was prepared by flow electrolysis in an apparatus constructed by Dr. G. Biedermann of this Department.[11]

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* Since, in the two-phase titrations, (practically) all HCl added to the system (before the equivalence point) was extracted into the organic phase, it might have been preferable to make the two latter solutions 1.000 M in LiCl for these experiments. On the other hand, the change in [Cl^-] is found to be negligible in practice.

The experimental technique

Emf-titrations. The experimental technique used, two-phase emf titrations, has been described in detail by Högfeldt.[9] An outline will be given here.

The measuring electrode is connected with the reference (Ag, AgCl) electrode through a "Wilhelm" bridge.[12]

Between the reference electrode and the titration vessel, the bridge is filled with ionic medium (1.000 M LiCl). The junction between the latter and the (aqueous) solution in the titration vessel is established by a fishhook-shaped capillary. The titration vessel contains ionic medium (initially 50 ml) and organic phase (10 – 25 ml). The measuring electrode (Beckman Blue glass electrode) dips into the aqueous phase. The apparatus is placed in a paraffin oil bath, thermostated at 25.00 ± 0.02°C, and standing in a room at 25 ± 0.5°C. (H+, Li+)Cl− solution is added from a calibrated buret. Stirring is done by means of a motor-powered glass stirrer.

To provide an inert atmosphere in the titration vessel, argon was slowly passed over the solutions. The argon had passed through 10 % NaOH, 1.00 M LiCl and amine-chloroform solution. (In some titrations with the higher amine concentrations, the vessel was merely filled with argon at the start of the titration. This was found to be quite satisfactory. Using either procedure for providing the argon atmosphere in two otherwise similar titrations (with 5 % DINA), practically identical $Z(\log h)$ "curves" were obtained; see below).

The emf (E) was measured with either a Radiometer PHM4 or a Metrohm E388 valve potentiometer. Both had been calibrated against a Cambridge Vernier potentiometer.

For each amine concentration at least two titrations were performed. For titration points before the equivalence point, the time for reaching equilibrium was usually 1 – 3 h (with vigorous stirring).

Before and after each titration a similar titration was carried out with no organic phase present in order to evaluate the characteristics ($E°$ and j, see below) of the glass electrode cell and to check that these had not changed appreciably during the titration.

The cell for the emf-measurements may be described schematically by

$$\text{Organic phase } \updownarrow$$
$$\text{Ag, AgCl(s)/1 M LiCl// } \quad \text{1 M (Li+, H+)Cl−/glass electrode}$$
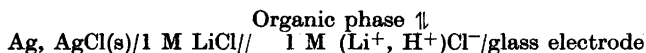
Assuming activity factors to be constant, the hydrogen ion concentration h was calculated from the equation

$$E = E° + 59.155 \log h + jh \tag{1}$$

The constants $E°$ and j (< 0) were determined from the titrations with no organic phase present.

Batch experiments. Samples of the organic solution (15 or 20 ml) were equilibrated with acid-water mixtures (usually 10 ml) of known composition by slow rotation for 2 h in stoppered bottles, in a room at 25.0 ± 0.5°C. (It was found that extending the shaking time to 4 h did not affect the results.)

Table 1. Concentrations of DINA in CHCl₃.

vol.%	moles·l⁻¹(M)
0.2	0.0061
0.5	0.0149
0.75	0.0216
1.0	0.0294
2.0	0.0587
5.0	0.1518
10.0	0.2950

At least two samples were prepared for each concentration of acid. The bottles were centrifuged for 5—10 min at 2500 rpm and aliquot portions were drawn from both phases for determination of their acid content (and of the water concentration in the organic phase).

The acid content in both phases was determined with standard NaOH, using methyl red indicator, within a few hours after centrifugation.

The water determinations were carried out according to Axel Johansson's [13a,b] modification of the Karl Fischer method, the titration carried out as a deadstop titration.

IR experiments. A Perkin-Elmer 421 double-beam instrument with NaCl cuvettes was used.

RESULTS

Preliminary experiments. Preliminary batch experiments showed that because of the rather limited solubility of the DINA hydrochloride, none of the hydrocarbons tried (neither aliphatic nor aromatic) would be a suitable solvent. Thus a more polar solvent, chloroform, had to be used, although this may involve the possibility of undesired solute-solvent interactions, rendering useful comparisons with the tertiary amine results available [2] more difficult.

Emf titrations. Seven concentrations of DINA, ranging from 0.2 % to 10 % by volume, have been studied. The corresponding molarities are given in Table 1.

The results are presented as Z_{HCl} as a function of $\log(h[Cl^-])$ where

$$Z_{HCl} = [HCl]_{org}/[DINA]_{tot} \qquad (2)$$

and $h \cdot [Cl^-]$ is the product of concentrations of H^+ and Cl^- in the aqueous phase. Since an ionic medium, 1.00 M $(Li^+, H^+)Cl^-$ was used, activity coefficients in the aqueous phase may be assumed to be practically constant, so that in equilibrium calculations the concentration product $h[Cl^-]$ can be used instead of the activity product.

The maximum deviation of $[Cl^-]$ from 1.00 M due to the extraction of HCl was 2—3 % (usually much less), which should not affect the activity factors appreciably (*cf.* Ref. 14). The extraction of LiCl is negligible ($\lesssim 10^{-4}$ M) as found in a check experiment in which 1 M LiCl was equilibrated with 10 % DINA in chloroform.

The experimental quantities Z_{HCl} and $\log(h[Cl^-])$ were evaluated in the following way. From the measured emf, E, $\log h$ was obtained, using eqn. (1). Since $[Cl^-] = 1.00$, $\log(h[Cl^-]) = \log h$. Then, the amount of H^+ in the organic phase, $n_{HCl(org)}$ mmoles, was computed from the known volume of the aq. phase, V_{aq}, and the amount of HCl added from the buret, $n^°_{H^+}$ mmoles, as:

$$n_{HCl(org)} = n^°_{H^+} - h \cdot V_{aq} \qquad (3)$$

The HCl in the organic phase is assumed to have complexed with DINA, and we use the relation

$$Z_{HCl} = n_{HCl(org)}/n^°_{DINA} \qquad (2b)$$

The number of millimoles of DINA, $n^°_{DINA}$, may be obtained in three ways:

a) from weighing, in the preparation of the amine solution;
b) by Gran's method [10] (see also Ref. 2);

c) from the approximately constant value reached by $n_{HCl(org)}$ at the end of a titration.

The methods b) and c) are related and depend on the fact that a distinct equivalence point is reached when $n°_{H^+}$ equals $n°_{DINA}$, that is, the composition of the organic phase reaches the composition DINA·HCl. The $n°_{DINA}$ value found from method a) usually was within $\sim 1 \%$ of the value found by methods b) and c). Normally a mean of the $n°_{DINA}$ values found by b) and c) was preferred.

The data, $Z_{HCl}(\log(h[Cl^-]))_B$, are given in Table 2, and in Fig. 1, Z_{HCl} is plotted against $\log(h[Cl^-])$ for the seven amine concentrations, B, studied. From Fig. 1 it is seen that Z_{HCl} is a function of both $h[Cl^-]$ *and* B, which indicates that one or more polynuclear complexes are formed.

Table 2. Equilibrium data for the extraction of HCl by B M DINA at 25.0°C and 1 M Li$^+$,H$^+$)Cl$^-$(aq) ionic medium, given in the form $\log(h[Cl^-])$,Z_{HCl}.

$B = 0.0061$ M.

−7.420,0.0323;	−7.247,0.0669;	−7.230,0.0671;	−7.098,0.1349;	−7.102,0.1358;
−6.990,0.2020;	−6.896,0.2709;	−6.735,0.4040;	−6.711,0.4066;	−6.568,0.5388;
−6.459,0.6106;	−6.378,0.6737;	−6.091,0.8086;	−5.859,0.8815;	−5.403,0.9507;
−5.197,0.9763;	−5.029,0.9788;			

$B = 0.0149$ M.

−7.748,0.0086;	−7.614,0.0324;	−7.425,0.0686;	−7.394,0.0689;	−7.320,0.1034;
−7.281,0.1356;	−7.201,0.1726;	−7.173,0.2060;	−7.083,0.2591;	−7.038,0.3095;
−7.016,0.3108;	−6.933,0.3797;	−6.874,0.4466;	−6.787,0.5167;	−6.757,0.5176;
−6.649,0.6208;	−6.470,0.6945;	−6.378,0.7735;	−5.849,0.9275;	

$B = 0.0216$ M.

−7.649,0.0463;	−7.357,0.1615;	−7.162,0.3243;	−7.156,0.3427;	−6.987,0.4601;
−7.000,0.4633;	−6.953,0.5070;	−6.862,0.5793;	−6.843,0.5798;	−6.782,0.6314;
−6.696,0.6945;	−6.664,0.6948;	−6.547,0.7582;	−6.238,0.8810;	−5.572,0.9725;

$B = 0.0294$ M.

−7.913,0.0138;	−7.786,0.0274;	−7.805,0.0340;	−7.619,0.0684;	−7.560,0.1052;
−7.371,0.2064;	−7.185,0.3445;	−7.004,0.4809:	−6.823,0.6180;	−6.608,0.7572;
−6.444,0.8228;	−6.415,0.8248;	−6.187,0.8935;	−6.047,0.9254;	−5.824,0.9581;
−5.724,0.9632;				

$B = 0.0587$ M.

−8.050,0.0068;	−7.979,0.0137;	−7.945,0.0340;	−7.790,0.0512;	−7.808,0.0693;
−7.644,0.1381;	−7.416,0.2410;	−7.340,0.3447;	−7.212,0.4130;	−7.171,0.4793;
−7.042,0.5509;	−6.987,0.6152;	−6.845,0.6894;	−6.752,0.7519;	
−6.513,0.8273;	−6.356,0.8885;			

$B = 0.1518$ M.

−8.383,0.0083;	−8.194,0.0166;	−8.160,0.0332;	−7.966,0.0662;	−7.954,0.0833;
−7.763,0.1497;	−7.705,0.1997;	−7.624,0.2659;	−7.572,0.3317;	−7.465,0.3990;
−7.394,0.4812;	−7.267,0.5658;	−7.110,0.6652;	−7.029,0.7355;	−6.882,0.7979;
−6.789,0.8354;	−6.557,0.8980;	−6.060,0.9645;		

$B = 0.2950$ M.

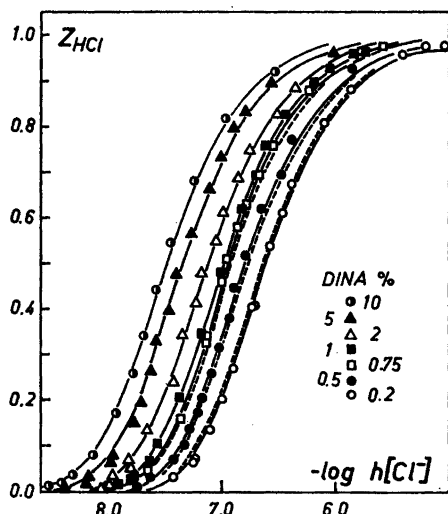|			
−8.528,0.008;	−8.410,0.017;	−8.312,0.034;	−8.128,0.077;	−7.928,0.169;
−7.780,0.255;	−7.688,0.340;	−7.580,0.442;	−7.448,0.544;	−7.245,0.681;
−6.968,0.817;	−6.532,0.919;			

Fig. 1. Z_{HCl} plotted against $-\log (h[Cl^-])$ for seven concentrations of DINA in chloroform. Ionic medium 1.00 M $(Li^+,H^+)Cl^-$.
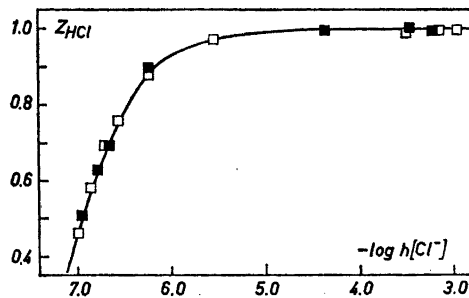

Fig. 2. Forward ($\square$) and back ($\blacksquare$) titration for 0.75 % DINA.

Reversibility of the reaction. In order to test the reversibility of the reaction a back titration with 5.35 mM LiOH, 994.6 mM LiCl was carried out for 0.75 % DINA. The two n°_{DINA} values found agreed within < 0.5 %. In Fig. 2, Z_{HCl} is plotted against $\log(h[Cl^-])$ for the forward and back titrations. It is seen that the points from the two titrations fall very nearly on the same average curve drawn through the data. Thus, it is concluded that the reaction is reversible.

TREATMENT OF DATA

A general reaction for the extraction may be written

$$q\text{DINA(org)} + p\text{H}^+\text{(aq)} + p\text{Cl}^-\text{(aq)} \rightleftharpoons (\text{DINA})_p(\text{HCl})_q\text{(org)} \qquad (4)$$
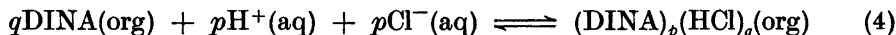
Any co-extraction of water cannot be evaluated from the emf data. Conductivity measurements, carried out by the author, indicate that ionic dissociation is negligible. ($\varkappa < 10^{-7}$ ohm^{-1}cm^{-1}).

Preliminary graphical treatment. From Fig. 1 it is seen that, besides not coinciding (thus indicating polynuclear complexes), the experimental "curves" seem to be parallel, at least in the range $0.2 < Z_{HCl} < 0.8$. This indicates the formation of "core-and-links" complexes,[15] $B(A_tB)_n$. or possibly a single complex (which can always be formulated as a core-and-links complex). In this case, B = DINA, A = HCl, and n is an integer. The parameter t may be found directly from the experimental data [15] as

$$t = -(\varDelta \log B / \varDelta \log h)_{z_{HCl}} \qquad (5)$$

The value obtained for t is, $t = 2.0 \pm 0.1$, corresponding to the series A_2B_2, A_4B_3, $A_6B_4 \cdots \rightarrow (A_2B)_n$. Only the first member of this series is compatible with the fact that, in the log h range studied, $Z_{HCl} \rightarrow 1$. The hypothesis of a single (2,2) complex was tested by the graphical methods given by Rossotti and Rossotti.[16] The result indicated a single (2,2) complex with a formation constant $k_{22} \approx 3.0 \times 10^{15} M^{-5}$.

The averages $\bar{p}$ and $\bar{q}$. In order to obtain additional, independent information about the composition of the complex(es) formed, a general integration method developed by Sillén [17] for the average composition ($\bar{p}$ and $\bar{q}$) of the complexes (A_pB_q) has been applied to the data.

Sillén's method does not involve any prior assumptions about the composition or formation constants of the complexes. The one assumption made is that the law of mass action (equilibrium law) is obeyed in its simple form. That is, activity coefficients are constant, and concentrations may be used in place of activities in the equilibrium law expression for reaction (4):

$$[(DINA)_q(HCl)_p]_{org} = k_{pq}[DINA]_{org}{}^q \cdot h_{aq}{}^p [Cl^-]_{aq}{}^p \qquad (6)$$

(This assumption is also implicit in all treatment of the emf data in this paper.)

For the aqueous phase this assumption is practically valid (see above). Assuming ideal behavior, it would hold in the organic phase also. This is reasonable; the highest amine concentration used (0.3 M) corresponds to a mole fraction, X_{DINA}, of merely 0.026. The scant information available on the activity of secondary long-chain amines in chloroform [31] seems to indicate that the activity factors may be fairly constant up to $X_{amine} \approx 0.01-0.05$. (Vapor pressure data [18] available for a few simple aromatic amines in chloroform, show deviations $\lesssim 1 \%$ from Raoult's law at ≈ 2.5 mole $\%$ amine.)

In conclusion the organic phase will be assumed to behave ideally. The simple mechanism obtained using this assumption may also be an argument in its favor (see below).

The calculations of $\bar{p}$ and $\bar{q}$ were performed with a computer using the program MESAK constructed by Sillén and Ingri.[19] The input data are simply the experimental $Z(\log h)_B$. The values for $\bar{p}$ and $\bar{q}$ for the first point ($\bar{p}_0$ and
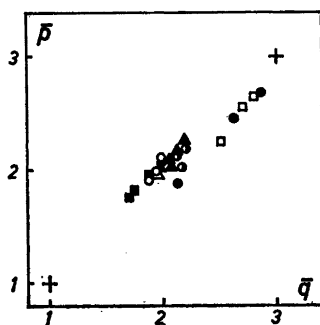

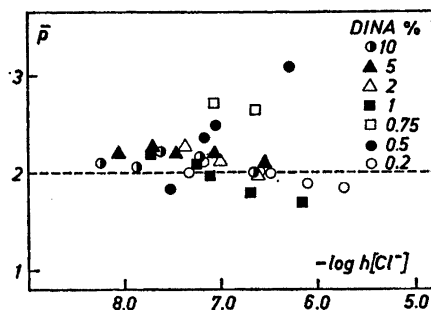*Fig. 3.* $\bar{p}$ plotted against $\bar{q}$ for various concentrations of DINA in chloroform.

Fig. 4. $\bar{p}$ plotted *versus* $-\log (h[Cl^-])$ for various concentrations of DINA in chloroform.

$\bar{q}_0$) are also required. This may be done by giving the computer estimated or guessed $\bar{p}_0$'s and $\bar{q}_0$'s. Alternatively one can have the computer estimate $\bar{p}_0$ and $\bar{q}_0$ by using the first two or three points to extrapolate backwards to find the integration constant related to $\bar{p}_0$ and $\bar{q}_0$. In either case, if a correct estimate of $\bar{p}_0$ and $\bar{q}_0$ has been used, a $(\bar{p},\bar{q})$ plot will produce a smooth curve, with no anomalous "bend" at the beginning.

Both methods were tried. In Fig. 3, $\bar{p}$ is plotted against $\bar{q}$ (using $\bar{p}_0 = \bar{q}_0 = 2$). It is seen that the values cluster around (2,2). When other $(\bar{p}_0, \bar{q}_0)$ values were tried, the points mostly converged rapidly at about $\bar{p} = \bar{q} = 2$. In Fig. 4, $\bar{p}$ ($\approx \bar{q}$) is plotted against $-\log(h[Cl^-])$ for the seven amine concentrations. (In this case $\bar{p}_0$ and $\bar{q}_0$ were estimated by the computer). In Figs. 3 and 4 there is some deviation towards (3,3) at two of the lowest concentrations, but this is contrary to the equilibrium law, and is likely to be caused by small systematic experimental errors.

Thus, also, the averages $\bar{p}$ and $\bar{q}$ hint mainly at a (2,2) complex.

Computer evaluation of the composition and formation constant(s) of the complex(es). In order to refine the mechanism suggested, the data were treated by a recent version of the general minimizing computer program LETAGROP.[20],[21] In this special case the error-square sum

$$U = \sum(Z_{calc} - Z_{exp})^2 \tag{7}$$

was minimized; Z_{calc} is the Z_{HCl} calculated using the mass balance for DINA and HCl, the equilibrium law expressions (6) for the complexes, and eqn. (2). Also a small systematic (*e.g.* analytical) error in Z_{HCl}, δZ, may be included.

The following complexes were tried: (2,2), (1,1), (0,2), (1,2), (2,1), and (3,3). All, except the (2,2), were rejected. As may be seen from Table 3, the formation constants, k_{pq}, of the other complexes (except (3,3)) either came out ≤ 0 or became $<$ their own standard deviations. In the case of (3,3) it was found that introducing and refining reasonable δZ values (see above) produced at least as good a fit as adding this complex. The δZ values found were of the order ± 0.001 to 0.02, which is quite reasonable in a system like this. (The higher δZ figures were obtained for the sets with the lowest B values where the accuracy is expected to be lowest.)

The final mechanism obtained (within the accuracy and the concentration range of the data) is thus the formation of a single dimer complex:

$$2DINA(org) + 2H^+(aq) + 2Cl^-(aq) \rightleftharpoons (DINA \cdot HCl)_2(org) \tag{8}$$
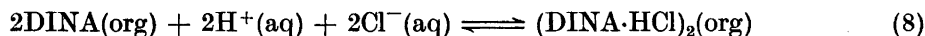
(org = chloroform solution; aq = 1 M (Li)Cl solution; $t = +25.0°C$)

$$k_{22} = (3.011 \pm 0.032) \ 10^{15} \ M^{-5} \tag{8b}$$

$$\log k_{22} = 15.479 \pm 0.014 \tag{8c}$$

The standard deviation $\sigma(k_{22})$ and the limits $\log(k_{22} \pm 3\sigma)$, are given.

In Fig. 1, Z_{HCl} (log h)$_B$ curves have been plotted, calculated from this mechanism, along with the experimental points. The dashed curves have been computed with all systematic errors, δZ, assumed to be zero. (This makes a difference discernible in the graph only at the three lowest B.)

Two-phase emf-titration combined with IR-spectrophotometry. Infra-red absorption spectra were obtained for the base form of DINA, pure, and in $CHCl_3$ and CCl_4 solution. In a comparison of spectra in these solvents, no

Table 3. Additional complexes, tried and rejected.

p	q	k_{pq}
1	1	$(0 \quad \pm 2.1) \times 10^{-2}$
1	2	$0 \quad \pm 700$
0	2	$(-9.5 \pm 8.1) \times 10^{-3} \approx 0$
2	1	$(0 \quad \pm 3.8) \times 10^4$
3	3	$(1.6 \quad \pm 0.3) \times 10^{23*}$

* $U = 4.14 \times 10^{-2}$ (all $\delta Z = 0$); *cf.* (2,2) complex, plus $\delta Z \neq 0$ ($\pm 0.001 - 0.02$): $U = 2.29 \times 10^{-2}$.

detectable evidence of specific interaction between DINA and $CHCl_3$ could be found. A (C—N stretching)[22,23] band at 1110 cm^{-1} was found to obey Beer's law for the DINA base form in $CHCl_3$ and CCl_4 to within $\lesssim 5$ %. This band did not appear either in DINA salt ($Z_{HCl} = 1$) solution or in solid DINAHCl(s). This is in agreement with the literature.[22,23] On the other hand, the protonated form of the amine produces a well-defined band ($-NH_2^+$ deformation) at 1585 cm^{-1}, also in agreement with the literature.[22,23] For this band, too, Beer's law appeared to be approximately valid (in $CHCl_3$). No frequency shift or band broadening with increasing concentration was observed. These observations in themselves would indicate a constant aggregation number within the concentration range studied. With both bands the "base-line method"[22] was used to estimate the extinction. (The following extinction coefficients were obtained in $CHCl_3$; $\varepsilon_{1110} \approx 50$ M$^{-1} \cdot$cm^{-1}; $\varepsilon_{1385} \approx 87$ M$^{-1} \cdot$cm^{-1}.)

These bands were used in conjunction with a two-phase emf-titration of 10 vol% DINA in $CHCl_3$ to obtain, along with h, approximate values for the concentrations (b and $[BH^+]$) of DINA base and "salt" form.

Samples of the organic phase (5 ml) were withdrawn at equilibrium, centrifuged, and their IR spectra recorded. The spectra of 10 % DINA base form ($Z_{HCl} = 0$) and "DINAHCl" ($Z_{HCl} = 1$) were also recorded and used as concentration standards. As reference solution pure chloroform (shaken with water) was used. No detectable difference using this reference instead of chloroform equilibrated with the proper HCl solution was found in check experiments.

(The Z_{HCl} values obtained from IR mostly agreed to within ± 0.01 with those from emf).

An attempt was made to check whether the IR-data of this (preliminary) experiment were consistent with the mechanism concluded from the emf results.

If just one complex, $(DINA)_q(HCl)_p$, (A_pB_q) is formed one has from the equilibrium law:

$$[BH^+] = q \cdot k_{pq} \cdot b^q \cdot h^p \cdot [Cl^-]^p \tag{10a}$$
$$([Cl^-] = 1)$$

Taking logarithms:

$$\log[BH^+] = \log(q \cdot k_{pq}) + q \cdot \log b + p \cdot \log h \tag{10b}$$

16
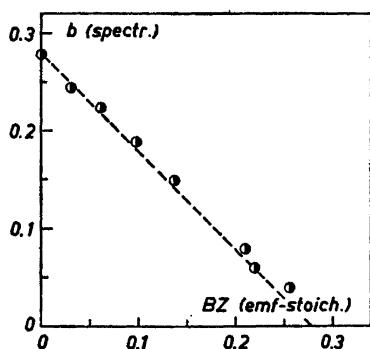
Fig. 5. b plotted against BZ for 10 %
DINA in chloroform. (IR spectroscopy
and emf data).
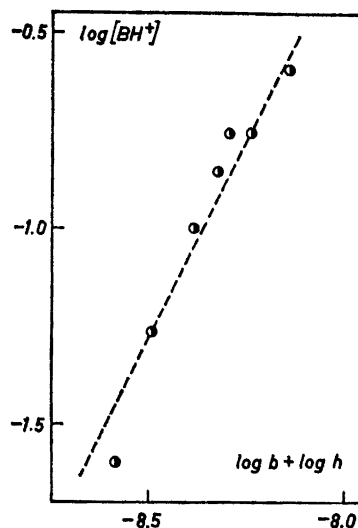
Fig. 6. log [BH+] plotted against (log
b + log h) for 10 % DINA in chloroform.
(IR spectroscopy and emf data).

If $p = q$ (one or more complexes) then it can easily be seen that

$$b = B - BZ \qquad (11)$$

This seems to hold, as may be seen from Fig. 5 where b (obtained from IR spectroscopy) has been plotted against BZ ($= n_{H^+(org)}/V_{org}$) obtained from the emf, using eqns. (1) and (3).

If $p = q$, eqn. (10a) suggests plotting log [BH+] versus (log b + log h). From Fig. 6 it is found that a straight line of slope ($= p = q$) ≈ 2 may be drawn through the points. The intercept corresponds to log $k_{22} \approx 15.5$.

A slope of unity is ruled out on the basis of the data.

The result of this experiment thus seems to be consistent with a (2,2) complex (at least at this concentration). With a more accurate IR-spectrophotometer available, the method of combining emf and IR (or other) spectral data may become of greater utility for this type of investigations. Its use for tertiary amines does not seem so promising, unfortunately, because of the lack of suitable absorption bands.[23]

Batch experiments. In order to investigate the range of acidity in which all amine has been converted to the salt, batch experiments have been performed with $HCl-H_2O$ mixtures in the range 0.3—11 M HCl. In Fig. 7, Z_{HCl} is plotted against the equilibrium molarity of HCl in the aqueous phase for the three concentrations 1, 5, and 10 vol%. From Fig. 7 it is seen that above $[HCl]_{aq} = 6$ M there is some excess extraction of HCl. The Z_{HCl} values are corrected for extraction by the diluent, chloroform. The extraction of water and hydrochloric acid by chloroform has been studied by Högfeldt and Fredlund,[24] and their results (plus a few of the author's own) have been

used in the computation of Z_{HCl} (including proper multiplication by the mole fraction of chloroform.) The extraction of HCl by chloroform (~ 0 at $[HCl]_{aq}$ < 6 M) increases very rapidly above $[HCl]_{aq} \approx 8$ M, making the corrections rather uncertain.
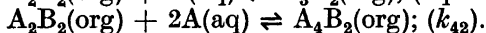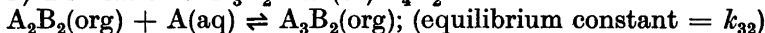
It is also seen from Fig. 7 that Z_{HCl} seems to be practically independent of the total DINA concentration, indicating that changes in aggregation are negligible.

The extraction of excess HCl. The following mechanisms were considered (A $= H^+Cl^-$; B $=$ DINA). (The HCl activities, $\{H^+\}\{Cl^-\}$, used have been taken from the compilation made by Högfeldt.[25])

1) Reactions involving changes in aggregation, *e.g.* formation of AB, or A_6B_4, etc.

Equilibria of this type would require a dependence of Z_{HCl} on the total concentration of B, this was not found experimentally.

2) Formation of A_3B_2 and (or) A_4B_2:
$A_2B_2(org) + A(aq) \rightleftharpoons A_3B_2(org)$; (equilibrium constant $= k_{32}$)
$A_2B_2(org) + 2A(aq) \rightleftharpoons A_4B_2(org)$; ($k_{42}$).

In the treatment of mechanism 2) normalized curves $y(\log u)^{26}$ ($y = Z_{HCl}-1$; $u = k_{32} \{H^+\}\{Cl^-\})$ were constructed for various values of the parameter, $p' = k_{32}(k_{42})^{-\frac{1}{2}}$, and compared with the data. It seemed that the "best" fit of the data was obtained for $p' \approx 2(\pm 1)$. The value $p' = 2$ corresponds to a "statistical distribution" of A between the two sites supposedly available on A_2B_2. In the "statistical" case, the probability that an A is attached to a certain site is independent of the situation at the other site.

The following formation constants were obtained ($\pm \sim 0.2$):

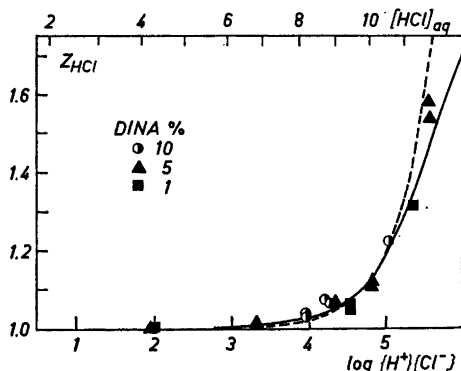$$\log k_{32} \approx - 5.62 \tag{12a}$$
$$\log k_{42} \approx -11.84 \tag{12b}$$

Fig. 7. Z_{HCl} plotted against $\log \{H^+\}\{Cl^-\}$ for 1, 5, and 10 % DINA in chloroform. Full curve, calculated using mechanism 2; Dashed curve, calculated using mechanism 3 (see text).
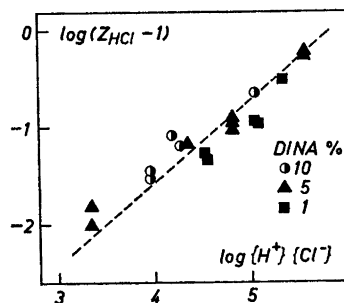
Fig. 8. $\log (Z_{HCl} -1)$ plotted against $\log \{H^+\}\{Cl^-\}$ for 1, 5, and. 10 % DINA in chloroform in the range $6-11.5$ M HCl(aq).

The complexes may or may not contain some water, but the experimental accuracy does not suffice to decide this question (*cf.* below, water extraction section).

3) Formation of complexes between the DINA salt and HCl, including species with $p/q > 2$ (more than one bonding site available per DINAHCl unit).

If there are $(Z_{max}-1)$ sites per AB unit, and the distribution is "statistical" (the sites take up A independently of each other) then the equilibrium law will give

$$\frac{Z_{HCl}-1}{Z_{max}-Z_{HCl}} = \text{constant} \cdot \{H^+\}\{Cl^-\} \tag{13}$$

The case with $Z_{max} = 2$ has been treated in 2) above.

For large values of Z_{max}, eqn. (13) approaches

$$Z_{HCl}-1 = k_1\{H^+\}\{Cl^-\} \tag{14}$$

where k_1 is a constant. Taking logarithms:

$$\log(Z_{HCl}-1) = \log k_1 + \log \{H^+\}\{Cl^-\} \tag{15}$$

In Fig. 8, log $(Z_{HCl}-1)$ is plotted against log $\{H^+\}\{Cl^-\}$ for 1, 5, and 10 vol% DINA, in the range $6-11.5$ M HCl(aq).

An average straight line of slope 0.9 may be drawn through the points. This is close to the slope of unity required from eqn. (15). The following average value for log k_1 was calculated:

$$\log k_1 = -5.40 \pm 0.10 \tag{16}$$

The same result was found, using a normalized curve

$$y(\log u), \text{ where } u = k_1\{H^+\}\{Cl^-\} \text{ and } y = Z_{HCl}-1.$$

A formally equivalent description is a distribution equilibrium

$$H^+(aq) + Cl^-(aq) \rightleftharpoons HCl.(org, DINAsalt) \text{ with the equilibrium "constant"}$$

$$k = k_1[\text{DINAsalt}] \tag{17}$$

The accuracy and available range of the data do not suffice to distinguish alternative ("statistical distribution") mechanisms of $Z_{max} \geq 2$. In Fig. 7, calculated curves for the limiting cases 2) $(Z_{max} = 2)$ and 3) $(Z_{max} \rightarrow \infty)$ have been plotted, together with the experimental points.

The extraction of water. The water extraction was also studied. However, the extraction of H_2O by the DINAHCl-chloroform solutions was not much higher than that by the diluent alone. (Typically, the diluent was responsible for ca 80 % of the total extraction.) The H_2O ascribed to extraction by "DINA HCl" is thus found as the difference between two nearly equal numbers. Consequently the $[H_2O]_{org}$ (or $Z_{H_2O} = [H_2O]_{org}(corr)/B$) values found are quite inaccurate and rather scattered (they are not shown here). The Z_{H_2O} values found ranged between 0.05 and 0.18, generally decreasing very slowly with increasing $[HCl]_{aq}$, *i.e.* decreasing H_2O activity. No quantitative mechanism can be offered on the basis of the data. The result of a few experi-

ments in the range $Z_{HCl} < 1$ may also be mentioned (5 % DINA in chloroform):

Z_{HCl}	Z_{H_2O}
0	0.10 (aq phase = pure water)
0.76	0.16

No definite stoichiometry seems to hold for H_2O.

A reasonable general (qualitative) conclusion seems to be that water plays no important part in the reactions between DINA and HCl in chloroform.

The solid, DINAHCl(s). The solid DINA hydrochloride — white in color — could be prepared by adding 0.1 M HCl(aq) to a 5 % solution of DINA in xylene. When produced by slow evaporation of an unsaturated solution it formed needle-like crystals. The crystallinity of the solid was confirmed by taking an X-ray powder photograph.

DISCUSSION

There seems to be no other detailed investigation, so far, of the build-up of a secondary amine to the corresponding salt. There is much evidence, however, from various experimental methods, that (strong) acid salts of long-chain secondary amines generally have a larger tendency to aggregate than the corresponding tertiary amine salts, solvent and other parameters being equal. Methods used in these findings include: light scattering,[27],[28] dipole moment measurements,[29] and (less consistently) extraction coefficient dependency studies by simple solvent extraction experiments.[1],[30] Also the solubility determinations and activity factor calculations by Kertes[31],[32] may be interpreted in such terms. On the other hand, the polar solvent (*e.g.* chloroform) and the strongly branched [25] carbon chains of the amine should give relatively less aggregation.*

In some systems, H_2O also may play part in the aggregation, although not in polar solvents (where H_2O may have to compete with solvating molecules). On the latter point, the findings of the present work seem to agree with those reported by Keder and Wilson [33] in the TOA-HCl-CHCl₃ system.

It should be noted that most of the work mentioned above has been confined to the acidity range in which all amine has been converted to the salt, whereas the present emf work has been concerned with the range in which base is transformed to salt ($Z_{HCl} > 1$). The recent emf results of Grinstead [34] confirm that no hint of a "mono-nuclear wall" is found for secondary amine-HCl systems (in toluene) in contrast to tertiary amine systems.

One may note also that in many secondary amine salt systems it has been found that the aggregation number (N) of the salt stays nearly constant over quite a large concentration range [27] (*cf.* also Ref. 32). (Examples from Ref. 27: $N \approx 4$ for a strongly branched sec. amine; $N \approx 40$ for a straight-chain sec. amine.)

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* *Note added in proof.* In a recent light-scattering study (Cattrall, R. W. and West, B. O. *J. Inorg. Nucl. Chem.* **29** (1967) 1145) an aggregation number between 1 and 2 is reported for the DINA sulfate in chloroform.

The absence of a dimer of the amine base form confirms the conclusions from IR-studies on secondary amines.[35],[36] (The generally rather weak tendency to dimerize being further counteracted by polar solvents and long carbon chains.)

A very notable feature of the simple (dimer) mechanism found is that it seems to hold even at $B = 0.3$ M; no corrections for non-ideality are needed. Thus, it seems that the activity coefficient ratio remains practically constant at least up to this concentration.

Comparisons with the results obtained in long-chain tertiary amine-acid systems by the two-phase emf titration method,[2] must be largely postponed until data are obtained from some tertiary amine-CHCl$_3$-acid-aq systems or secondary amine-(aromatic)hydrocarbon-acid-aq systems.

Further, X-ray study of solutions and single crystals of the amine salt would be of great interest; as well as metal (an)ion extraction (which may also be studied by means of two-phase emf-titrations in suitable systems [37],[38]).

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