

Aggregation of Di(isononyl)ammonium Chloride in Chloroform Solution, and Extraction of Zinc Chloride

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The aggregation of a secondary aliphatic ammonium salt, di(3,5,5-trimethyl)ammonium chloride, $[(\text{CH}_3)_3\text{C}_6\text{H}_{10}]_2\text{NH}_2\text{Cl}$, "DINAHCl", in dry chloroform has been studied by osmometric measurements. The data indicate that the ammonium salt in this solvent exists as a dimer $(\text{DINAHCl})_2(\text{org})$ only. This result is consistent with that of an earlier emf study.¹ Distribution data for a metal ion, Zn^{2+} , between 1 M $(\text{H}^+)\text{Cl}^-(\text{aq})$, and DINAHCl in CHCl_3 , are in agreement with a constant aggregation number for the ammonium salt.

In a previous communication^{1*} the results of a study, mainly by two-phase emf measurements, on the system diisononylamine (=DINA = di(3,5,5-trimethylhexyl)amine)-HCl- CHCl_3 - H_2O (1 M LiCl) were presented. Within the concentration range and the accuracy of the data practically all the ammonium salt formed in the organic phase was found to be dimeric, $(\text{DINAHCl})_2$. In this paper a further study using osmometry is reported together with some distribution experiments with zinc chloride.

EXPERIMENTAL

Chemicals. For DINA and HCl, see Ref. 1a. Chloroform (Merck, *p.a.*) was shaken 3-4 times with water to remove the ethanol. For osmometry it was desiccated on an alumina column. The amount of water present after desiccation was checked by Karl Fischer titration, and found to be less than 1 mM, close to the detection limit of the method.

DINAHCl(s) was prepared as described previously.¹ It was recrystallized twice from hexane. For the osmometric study it was dried over P_2O_5 . Zinc chloride (Merck, *p.a.*) was used without further purification. All aqueous solutions were prepared using doubly distilled water.

Zinc-65 chloride was obtained from Amersham, England, in the form of an 0.0223 M solution in 0.1 M HCl.

* A misprint in Ref. 1a should be corrected: Near the bottom of page 1365, read ($Z_{\text{HCl}} < 1$) ...

Osmometric measurements were made at 25.0°C using a Mechrolab Vapor Pressure Osmometer Model 301A and at 30°, 35° and 40°C using a Hitachi Perkin Elmer Molecular Weight Apparatus, Model 115. The resistance difference, ΔR , between matched thermistors, one with a drop of solution, the other with solvent, was recorded every minute, 2–12 min after application of the solution drop. Runs were made at least in duplicate with each solution in order to check reproducibility. Distribution experiments: Solutions in stoppered tubes of ZnCl_2 in $1 \text{ M}(\text{H}^+)\text{Cl}^-$ (10.0 ml) were equilibrated with DINAHCl in CHCl_3 (10.0 ml) by slow rotation. After centrifugation, aliquots were withdrawn from each phase for γ counting. All experiments were made in a room thermostated at $25 \pm 0.5^\circ\text{C}$.

OSMOMETRIC RESULTS

Solutions of DINA chloride in chloroform were studied, as well as solutions of DINA (base) and of benzil (as standard) in the same solvent.

ΔR values taken at a constant time = 12 min after application of the solution drop were used (ΔR values obtained by extrapolating experimental ΔR vs. time curves to time = 0 were found not to produce significantly different final results; cf. below). The results are shown in Fig. 1 as a plot of $\Delta R/C$

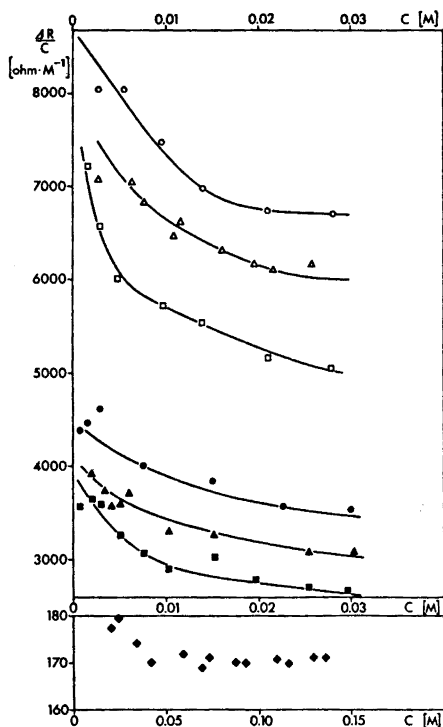


Fig. 1. $\Delta R/C$ plotted versus C for DINAHCl (filled symbols) and benzil (open symbols) in chloroform. \blacksquare , \square , 40°C. \blacktriangle , \triangle , 35°C. \bullet , \circ , 30°C. \blacklozenge , \lozenge , 25°C. ($\Delta R/C$ for DINA at 25°C = 315 ± 3 .) Averaged calibration curves drawn through the benzil points. Average curve corresponding to $\bar{n} = 2$ drawn through the DINAHCl points at 30–40°C.

vs. C where C is total concentration in M (mol l^{-1}). See also Table 1. The amine base form, DINA, gave very nearly the same results as benzil, *i.e.*, it may be regarded as monomeric in chloroform solution.

Table 1. Osmometric data for DINAHCl in CHCl₃, given as C , ΔR .

25°C:	0.1353, 23.14; 0.1280, 21.90; 0.1152, 19.60; 0.1082, 18.48; 0.0922, 15.75; 0.0866, 14.72; 0.0735, 12.55; 0.0693, 11.65; 0.0588, 10.10; 0.0416, 7.06; 0.0333, 5.80; 0.0235, 4.22; 0.0200, 3.55;
30°C:	0.03013, 106.94; 0.02276, 80.94; 0.01506, 57.80; 0.00753, 30.06; 0.00301, 13.90; 0.00151, 6.72; 0.00075, 3.30;
35°C:	0.03038, 94.06; 0.02550, 78.34; 0.01519, 49.74; 0.01020, 33.70; 0.00608, 22.60; 0.00510, 18.32; 0.00409, 14.60; 0.00304, 11.30; 0.00204, 8.00; 0.00127, 6.16;
40°C:	0.02952, 78.70; 0.02538, 69.16; 0.01972, 55.00; 0.01527, 46.10; 0.01026, 29.50; 0.00763, 23.35; 0.00513, 16.74; 0.00305, 10.96; 0.00205, 7.54; 0.00076, 2.72.

The following equations apply:

$$\Delta R = k_{R1}S + k_{R2}S^2 \quad (1)$$

$$S = c + K_2c^2 + \dots + K_n c^n \quad (2)$$

$$C = c + 2K_2c^2 + \dots + nK_n c^n \quad (3)$$

$$\bar{n} = C/S \quad (4)$$

where k_{R1} and k_{R2} are proportionality factors, which may usually be considered constant at constant temperature for a given solvent; S is the concentration of solute molecules, in M; c is the concentration of monomeric solute, in M; \bar{n} is the average aggregation number; K_n is the equilibrium constant for the reaction



where A is the solute. The parameters, k_{R1} and k_{R2} , were evaluated from measurements with benzil (and DINA at 25°C). Preliminary calculations indicated, in agreement with previous results,¹ that $\bar{n} \approx 2$ over the whole concentration range studied and that values of $n > 2$ need not be considered.

In the calculations a version^{2c} of the general minimization program LETAGROP² was employed. The quantity (error squares sum) minimized was either

$$U_1 = \sum (\Delta R_{\text{calc}} - \Delta R)^2 \quad (5a)$$

or

$$U_2 = \sum ((\Delta R_{\text{calc}} - \Delta R)/\Delta R_{\text{calc}})^2 \quad (5b)$$

where the sum was taken over experimental points in the C range $7 \times 10^{-4} - 3 \times 10^{-2}$ at each of the temperatures 30, 35, and 40°C, and in the range 0.02–0.15 M at 25°C. ΔR_{calc} was computed using eqns. (3), (2), and (1). These calculations indicated that within accuracy of the data diisononylammonium chloride is dimeric in chloroform, *i.e.* it was found that $K_2 \geq 10^6 \text{ M}^{-1}$ at 30–40°C. (The results obtained with the Mechrolab Osmometer in the range $C < 0.02$ M at 25°C suggested some monomer formation.^{1b} These data were found to be of lower precision, however, and were not included in the final treatment of the material.)

However, the computer program available^{2c} does not, at present, allow a strict evaluation of curved plots of $\Delta R/C$ vs. C of the type found experimentally both for benzil and DINAHCl, at 30–40°C (*cf.* Fig. 1). Such a case

may be dealt with either by adding higher-order term(s) to the right hand side of eqn. (1), or by fitting an exponential calibration curve.³

A third possibility is the evaluation of \bar{n} from

$$\bar{n} = (\Delta R/C)_{\text{ref}} / (\Delta R/C)_{\text{DINAHCl}} \quad (6)$$

at each individual C value; *i.e.*

$$\bar{n} = \frac{k_{R1}(C) + k_{R2}(C)C}{k_{R1}(C)\bar{n}^{-1} + k_{R2}(C)C\bar{n}^{-2}} \quad (7)$$

where it has been indicated that k_{R1} and k_{R2} (obtained from the monomeric calibration substance, *e.g.*, benzil) may vary with C .

Eqn. (7) becomes a simple identity if $k_{R2}(C) = 0$ for all C values, and eqn. (6) may then be applied directly. This was the case for the data at 25°C. Data at the other temperatures were treated by applying eqn. (7) iteratively. The resulting final \bar{n} values have been plotted as a function of C in Fig. 2; it is

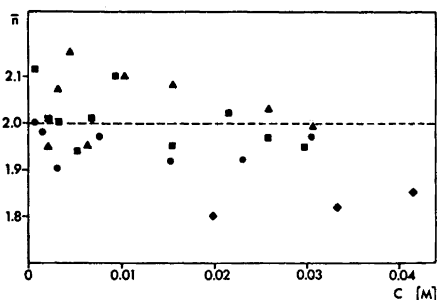


Fig. 2. Mean aggregation number, \bar{n} , plotted as a function of C for DINAHCl in chloroform at temperatures 25–40°C. Same symbols as in Fig. 1. (Points at 25°C with C values 0.05–0.14 M all have \bar{n} values in the range 1.82–1.86.)

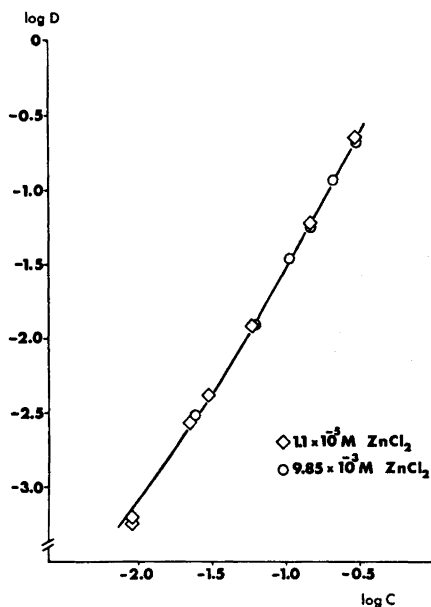


Fig. 3. Log of distribution ratio for ZnCl_2 between chloroform and 1 M $(\text{H}^+)\text{Cl}^-(\text{aq})$ as a function of $\log C$ (DINAHCl) at 25.0°C. The curve has been computed using $K_{11}' = 0.1108 \text{ M}^{-1}$ and $K_{12}' = 9.40 \text{ M}^{-2}$.

seen that, within the limits of error ($\pm 5\%$ at 30–40°C; $\pm 10\%$ at 25°C), $\bar{n} = 2$ at all C values and temperatures considered. From the experimental error limits the following lower limits for K_2 can be estimated:

and $K_2 \gtrsim 10^5 \text{ M}^{-1}$ at $30 - 40^\circ\text{C}$ ($C \gtrsim 0.001 \text{ M}$)
 $K_2 \gtrsim 2 \times 10^3 \text{ M}^{-1}$ at 25°C ($C \gtrsim 0.02 \text{ M}$)

DISTRIBUTION OF ZnCl_2

The distribution equilibrium of ZnCl_2 between an organic phase, $C \text{ M}$ DINAHCl in CHCl_3 , and an aqueous phase, Zn^{2+} in 1.00 M $(\text{H}^+)\text{Cl}^-$, has been studied. Two different initial concentrations of $\text{ZnCl}_2(\text{aq})$, $1.1 \times 10^{-5} \text{ M}$ and $1 \times 10^{-2} \text{ M}$ were used, and C was varied throughout the range $0.01 - 0.3 \text{ M}$. The data have been plotted in Fig. 3 as $\log D_{\text{Zn}}$ vs. $\log C$, where

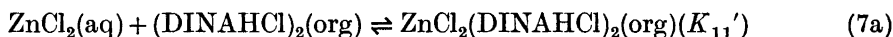
$$D_{\text{Zn}} = \frac{[\text{ZnCl}_2(\text{org})]}{[\text{ZnCl}_2(\text{aq})]} = \frac{{}^{65}\text{Zn activity}(\text{org})}{{}^{65}\text{Zn activity}(\text{aq})} \quad (6)$$

See also Table 2.

Table 2. Distribution data for Zn(II) between 1 M $(\text{H}^+)\text{Cl}^-$ and $C \text{ M}$ DINAHCl in CHCl_3 at 25°C , given as C, D_{Zn} ; where D_{Zn} is the average of two determinations (cf. Fig. 3).

$[\text{Zn}(\text{II})]$ (initial) = $1.11 \times 10^{-5} \text{ M}$:	0.0091, 0.00060; 0.0227, 0.00266; 0.0297, 0.0040; 0.0300, 0.00397; 0.0600, 0.0120; 0.149, 0.0595, 0.298, 0.2222;
$[\text{Zn}(\text{II})]$ (initial) = $9.85 \times 10^{-3} \text{ M}$:	0.0242, 0.00294; 0.0605, 0.0118; 0.1059, 0.0337; 0.1482, 0.0568; 0.2117, 0.1150; 0.2965, 0.211.

The experimental points in Fig. 3 all seem to fall on a nearly straight line with slope ≈ 1.7 , independent of ZnCl_2 concentration. This would suggest that ZnCl_2 is extracted in the form of homo-nuclear complexes with n and (mainly) $2n$ DINAHCl units; according to the osmometric results, $n = 2$:



In addition, we have the equilibria between Zn^{2+} and Cl^- in the aqueous phase. Since, however, the $\text{Cl}^-(\text{aq})$ concentration is constant the proportions of $\text{Zn}^{2+} - \text{Cl}^-$ complexes in the aqueous phase are constant, and correspond to a constant factor included in K_{11}' and K_{12}' .

A preliminary graphical treatment of the data indicated $K_{11}' = 0.136$ and $K_{12}' = 9.3$. The data were then treated by a special version of the LETAGROP program,^{2,4} minimizing the quantity

$$U = \sum (\log D_{\text{Zn}}(\text{calc}) - \log D_{\text{Zn}})^2$$

The full drawn curve in Fig. 3 has been calculated using the following values, obtained in the LETAGROP treatment:

$$K_{11}' = 0.1108 \pm 0.0052 \text{ M}^{-1}$$

$$K_{12}' = 9.40 \pm 0.21 \text{ M}^{-2}$$

(The standard deviations (σ) are quoted.)

It is worth mentioning that as long as the aggregation number is constant the system can be treated formally as a mononuclear one.

DISCUSSION

The dimeric state of DINAHCl in chloroform found in this work is consistent with the previous two-phase emf work¹ at 25°C.

Besides the present work, and Ref. 1, the only published study of secondary ammonium halides in chloroform seems to be that by Casey *et al.*⁵ Their two-phase emf titrations and v.p. osmometry data for dilaurylammonium halides, DLAHX, were explained in terms of a monomer-dimer equilibrium; K_2 (cf. eqns. (2) and (3)) being $400 \pm 100 \text{ M}^{-1}$ for $\text{X}^- = \text{Cl}^-$ at 25°C; lower K_2 values were found for $\text{X}^- = \text{Br}^-$ and I^- .

The aggregation of long-chain ammonium salts in chloroform does not seem to proceed beyond dimers in the systems studied so far,^{6a} and the results in this paper are consistent with these results. A comparison with the results of Casey *et al.* shows that DINAHCl has a larger dimerization constant than DLAHCl. Perhaps the branching of the hydrocarbon chains in DINAHCl permits less interaction with the solvent, thus promoting dimerization.

In the general case the degree of association varies with composition.^{6b,7,8} Nevertheless, metal extraction as well as excess acid extraction is often "best" described with mononuclear complexes only, a fact which still remains to be fully understood.

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