four runs, -8420 ± 400 cal./mole, has been taken to represent the heat of reaction of α-$Na_2N_2O_3$ in its standard macrocrystalline state.

Discussion

From the measured value of the heat of formation of α-$Na_2N_2O_3$ in 0.1 *m* NaOH solution and the standard heats of formation of sodium ion ($-57,279$) and $N_2O_2^{-2}$ ($-2,590$) in dilute aqueous solution given by Rossini, Wagman, Evans, Levine, and Jaffe,[5] ΔH has been calculated for the process

$$\alpha\text{-}Na_2N_2O_3(aq) = Na_2N_2O_2(aq) + {}^1/_2O_2(g); \quad \Delta H = +20{,}000 \text{ cal.}$$

The heat associated with removal of 1/2 O_2 from $NaON^{O}_{O}(aq)$ to form $NaNO_2(aq)$ is calculated from the heat of this reaction for crystalline $NaNO_3$ and $NaNO_2$ [$(+24{,}900)^9$], and the standards heats of solution of $NaNO_3(c)$ $(+4{,}889)^5$ and $NaNO_2(c)$ $(+3{,}320)^{10}$

$$NaON^{O}_{O}\,(aq) = NaNO_2(aq) + {}^1/_2O_2; \quad \Delta H = +23{,}331 \text{ cal.}$$

Since the heat of rearrangement of NaONOO(aq) to $NaONO_2(aq)$ is $-34,000$ cal.,[11] it follows that

$$NaONOO(aq) = NaNO_2(aq) + {}^1/_2O_2; \quad \Delta H = -10{,}969 \text{ cal.}$$

By analogy, removal of 1/2 O_2 from an $Na_2ON^{O}_{O}$ structure would give a ΔH of approximately +23,000, and removal of 1/2 O_2 from Na_2ONNO–O should give ΔH of $-11,000$. Since the actual value is +20,000, the $Na_2ON^{O}_{O}$ structure is suggested.

Acknowledgments.—This research was supported in part by a grant from the Research Corporation and in part by a grant (NSF-G15560) from the National Science Foundation.

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Notes

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An X-Ray Diffraction Study of Aqueous Zinc Chloride Solutions[1]

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Received December 8, 1961

The solubility of zinc chloride in water is so great that the mole ratio of water to zinc chloride can easily be made smaller than 2:1 even at room temperature. At such high concentration it becomes a semantic question as to whether the system is called a solution or a molten salt, and unusual physical properties suggest interesting structural features whose nature might be deduced from diffraction data.

High viscosity, low electrical conductivity, and behavior in extraction experiments all suggest polymerization in concentrated solution. The great increase in viscosity[2] with increasing concentration cannot be accounted for in terms of simple species, and extraction into 2-octanol[3] shows less than one water molecule per zinc ion. One therefore suspects, if he assumes at least four-coördination for zinc, the existence of some polynuclear species in which chlorines are shared. Indeed, four-coördination of zinc by chlorine occurs in crystalline zinc chloride[4] and in solutions containing zinc chloride together with an added chloride,[5–7] but it remains to test the assumption in the system $ZnCl_2$–H_2O and to establish the identity of the ligands.

(1) The support of the U. S. Atomic Energy Commission is gratefully acknowledged.

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To find out about the coördination of zinc we measured[8] the X-ray intensity diffracted ($s_{max} = 14.00$ Å.$^{-1}$) by the following solutions at room temperature (m = molality)

27.5 m	$Zn_{0.20}Cl_{0.40}(H_2O)_{0.40}$
8.5 m	$Zn_{0.11}Cl_{0.22}(H_2O)_{0.67}$
5.0 m	$Zn_{0.07}Cl_{0.14}(H_2O)_{0.79}$

Intensity was corrected for background, polarization, absorption, and incoherent scattering. Radial distribution curves are shown in Fig. 1.

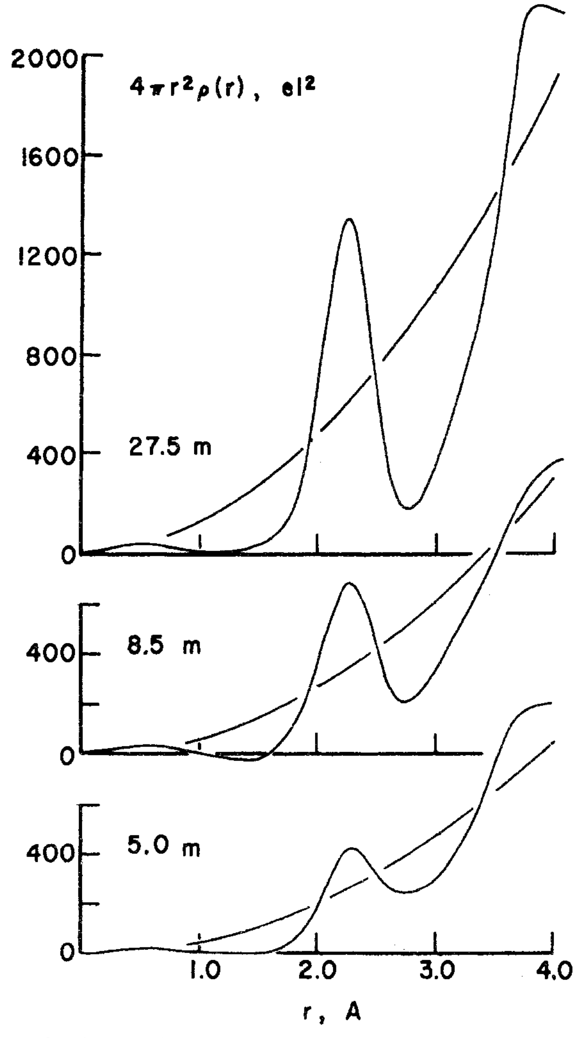

Fig. 1.—Radial distribution functions for zinc chloride solutions. Molality is given at left of each curve. The smooth curves are $4\pi r^2\rho_0$, the function corresponding to a uniform distribution of X-ray scatterers within the solutions. The contribution of hydrogen atoms to ρ_0 is omitted.

Results

For all three solutions the first maximum in the radial distribution function (RDF) occurs at 2.28 Å., which agrees with zinc–chlorine distances in crystalline zinc chloride[4] and in the tetrachlorozincate ion.[9] For the 27.5 and 8.5 m solutions this peak is fairly well resolved, and its area can be reliably assigned. The area of 700 el^2 found for the 27.5 m solution lies between the values expected[10] for three chlorines and four chlorines per zinc, namely 607 and 810 el^2. In fact, this area (700 el^2) is exactly what is expected for three chlorine and one oxygen (water) per zinc.

Figure 2 shows that a first maximum calculated[10] on this basis agrees with that observed. Moreover this assignment agrees roughly with extraction experiments,[3] which show that for aqueous molalities above 7 there is 0.8 water molecule per zinc extracted into 2-octanol. We conclude that, on the average, each zinc has one water and three chlorine neighbors in 27.5 m solution. Figure 2 shows that the same assignment satisfactorily accounts for the 8.5 m solution as well. The results for these solutions support the assumption of four-coördination.

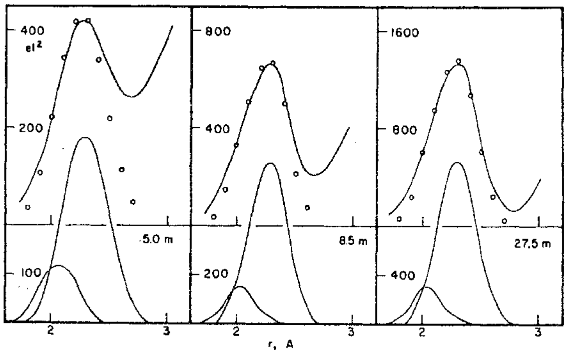

Fig. 2.—A comparison of calculated and observed first maxima in the radial distribution functions. For each solution two component peaks, a zinc–chlorine peak at 2.28 Å. and a zinc–oxygen peak at 2.05 Å., are added to give the calculated peak, and these components (see text) are shown in the lower diagrams. In the upper pictures the sums of these components (represented by circles) are compared with the observed maxima.

The interpretation of the RDF for the 5.0 m solution depends on a judgment as to how much area should be associated with the first peak, which is not at all well resolved. If we arbitrarily extrapolate the left hand side of the second peak to the abscissa there remains an area of

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230 el^2 under the first peak. Even though this estimate may be in error by 10 to 15%, its magnitude and the position of the peak indicate that dilution to 5.0 *m* does not bring about extensive replacement of chlorines by water, but it must be admitted that the results for this solution are ambiguous and do not provide a unique determination of the coördination number for zinc. An assignment of area based on four-coördination leads to a reasonable picture, however.

On this assumption, we find that the area of the first peak lies between the values expected for two water–two chlorine neighbors and for one water–three chlorine neighbors per zinc, namely 216 and 250 el^2. The average coördination of zinc therefore would consist of about 2.4 chlorine and 1.6 water neighbors in 5.0 *m* solution. For this concentration, extraction measurements[3] indicate 2.2 waters per zinc.

Discussion

The results show that in very concentrated solution zinc has a coördination number of four and that its coördination is very much like that in crystalline zinc chloride, with water substituted, however, for part of the chlorine. There is a suggestion that the coördination is tetrahedral, as it is in the crystal, since there is a maximum in the RDF at about $\sqrt{8/3} \times 2.8 = 3.72$ Å. On the other hand, it must be admitted that, at least for the 27.5 *m* solution, chlorine–chlorine contacts would occur in this range regardless of the coördination of the zinc.

For the 27.5 and 8.5 *m* solutions, consideration of stoichiometry (two chlorines per zinc) and diffraction data (one water and three chlorine neighbors per zinc) makes inescapable the conclusion that half the chlorines, on the average, are shared between zincs. Assuming that all zincs are equivalent we therefore may describe the average coördination of zinc in solution in terms of $Zn(H_2O)Cl_2$ units which are coupled through one of the two chlorines per zinc. Any other description requires non-equivalence of zincs or the sharing of more than one chlorine per zinc. Although the RDF does not furnish enough detail about second nearest neighbors to permit a discussion of extended or long range structure, we believe that the results show convincingly the existence of shared ligands and that they provide a basis for understanding some of the unusual properties of the solutions.

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Boron–Nitrogen Compounds. VII.[1,2] B-Trifluororobazine

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Received March 26, 1962

B-Trichloro- and B-tribromoborazine $(-BX-NH-)_3$ are well known compounds and can be prepared by several methods.[3] B-Trifluoroborazine, however, has not been described in the literature. As a matter of fact, the knowledge of B-fluorinated borazines is extremely limited: B-trifluoro-N-trimethylborazine first was obtained on thermal decomposition of the methylamine adduct of dimethylfluoroborane[4]; B-trifluoro-N-trisilylborazine has been mentioned in the literature,[5] but no supporting data or analysis were presented; a vapor pressure of 5.9 mm at 24.1° was recorded for a material believed to be B-difluoro-N-trimethylborazine.[6] A more recent attempt to prepare fluorinated borazines resides in the interaction of diborane and tetrafluorohydrazine,[7] but has yet to be demonstrated as a preparative method. All this available information makes it appear that B-fluorinated borazines are either difficult to prepare or relatively unstable materials.

It now has been found that B-trifluoroborazine can be prepared easily through transhalogenation of B-trichloroborazine. The latter is commercially available[8] and a number of its reactions have been studied.[3] Halogen exchange at the boron atom, however, has not been reported.

Several fluorinating agents have been found suitable for the reaction

$$(-BCl-NH-)_3 + 3MF \rightarrow (-BF-NH-)_3 + 3MCl \quad (1)$$

where M is a metal ion. Potassium fluoride yielded small amounts of the desired product after extensive refluxing in high boiling solvents; isolation of the B-trifluoroborazine from the reaction mixture proved to be a difficult and tedious procedure.

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