melting point of these preparations checked to within 0.1° with the literature values.

Solvents and Solutions.—Ethylene dichloride was purified by a previously described method.[4] The boiling point of the purified solvent was 83° at 750 mm. pressure. The specific conductance of the solvent was found to be less than 10^{-9} ohm $^{-1}$ cm.$^{-1}$ and was too low to necessitate any corrections even for the most dilute solutions.

Approximately 10^{-2} M stock solutions were prepared by dissolving a weighed amount of solute in an appropriate amount of solvent. Dilutions were made by the addition of a known amount of the stock solution from a weight buret to the solvent. This technique was found to be more accurate than the usual dilution method since solutions down to 10^{-5} M had to be prepared. All of the solutions were found to be stable for at least 24 hours, but the measurements were made on the solutions prepared on the same day.

Results and Discussion.—Equivalent conductances obtained for the polyhalide solutions are tabulated in Table I where a typical series of measurements are given. Several runs were made on different sets of solutions, but the results agreed within experimental error.

TABLE I

EQUIVALENT CONDUCTANCES OF POLYHALOGEN COMPLEXES IN ETHYLENE DICHLORIDE AT 25°

$c \times 10^4$	Λ	$c \times 10^4$	Λ
$(CH_3)_4NIBrCl$		$(n\text{-}C_3H_7)_4NIBr_2$	
0.6074	53.00	0.5185	56.20
1.367	43.88	1.306	48.86
2.217	38.27	2.242	44.12
5.727	28.41	2.972	41.45
7.582	25.93	3.720	39.35
9.277	24.24	7.258	33.30
27.02	20.74	9.013	31.64
$(n\text{-}C_4H_9)_4NBr_3$		$(n\text{-}C_4H_9)_4NICl_2$	
0.3689	52.70	0.1651	58.98
0.9208	47.20	1.199	47.68
1.667	42.54	2.717	40.59
2.566	38.69	4.467	36.22
3.614	35.76	7.132	32.22
8.513	28.59	14.49	26.79
17.99	23.23		

Plots of $\sqrt{c}$ *vs.* Λ deviated considerably from straight lines showing appreciable ion-pair association especially in the more concentrated solutions.

The data were treated by the method of Fuoss and Kraus.[5] The F/Λ *vs.* $c\Lambda f^2/F$ plots gave in each case satisfactory straight lines. The intercepts of the lines yield $1/\Lambda_0$ and the slopes $1/K\Lambda_0^2$. The calculated values of the limiting conductance and of the ion-pair dissociation constants are given in Table II.

TABLE II

CONDUCTANCE DATA IN ETHYLENE DICHLORIDE

Complex	Λ_0	$\lambda_0^{+\,a}$	λ_0^-	$K \times 10^4$
$(CH_3)_4NIBrCl$	81.6	42.6	39.0	0.68
$(n\text{-}C_3H_7)_4NIBr_2$	68.3	31.5	36.8	2.11
$(n\text{-}C_4H_9)_4NBr_3$	62.2	26.2	36.0	2.05
$(n\text{-}C_4H_9)_4NICl_2$	64.5	26.2	38.3	2.27

[a] Reference 6.

Since the limiting conductances of the tetramethylammonium, n-tetrapropylammonium and n-tetrabutylammonium cations in ethylene dichloride at 25° have been determined by Tucker and Kraus,[6] it is possible to calculate the limiting equivalent conductances of the polyhalogen ions used in this investigation.

The results are likewise given in Table II. As ionic mobilities are equal to $\lambda^{\pm}/F$, the mobilities of the polyhalogen ions come in the following sequence, $IBrCl^- > ICl_2^- > IBr_2^- > Br_3^-$ but the actual differences are rather small, which indicates that the ions are of approximately the same size.

Acknowledgment.—The authors gratefully acknowledge the support of this work by the Research Corporation.

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[4] A. I. Popov and R. F. Swensen, THIS JOURNAL, **77**, 3724 (1955).

[5] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 476 (1933); R. M. Fuoss, *ibid.*, **57**, 488 (1935).

[6] L. M. Tucker and C. A. Kraus, *ibid.*, **69**, 454 (1947).

The Lowering of the Freezing Point of Sodium Hydroxide on Addition of Salts

BY R. P. SEWARD

RECEIVED JUNE 17, 1955

From calorimetric measurements, Douglas and Dever[1] have found the heat of fusion of sodium hydroxide to be 1520 ± 5% cal. per mole. These authors suggest that the figure of 1670 cal. per mole, calculated by the writer[2] from freezing points in the $NaOH$–Na_2CO_3 system, is in error because the effective molecular weight of Na_2CO_3 in solution may deviate from its formula weight. As the value from the freezing point measurements was calculated from temperatures determined to the nearest degree and the greatest lowering employed was 13°, it is quite probable that the discrepancy is due to the lack of precision in the freezing point data.

Subsequent to the observations on the $NaOH$–Na_2CO_3 system, the writer determined the lowering of the freezing point of sodium hydroxide on addition of $NaBr$, KBr, K_2CO_3 and again Na_2CO_3. While these measurements too are not of sufficient precision to define the heat of fusion accurately, it is thought that they may be of interest for their bearing on the extent of dissociation and ideal behavior in fused salt solutions.

The data on the lowering of the freezing point of sodium hydroxide are tabulated below. ΔT is the observed lowering, N is the ratio of the number of formula weights of solute to total formula weights, and i is the ratio of the observed lowering to $460N$. The mole fraction freezing point lowering constant, $RT^2/\Delta H_F$, using 1520 cal. per mole for ΔH_F, has a value of 460.

Within the precision of the measurements, it appears that the above data are consistent with complete dissociation of solute and solvent and ideal behavior; one formula weight of solute contributing one mole of solute ion in the case of Na_2CO_3 and $NaBr$, two moles of solute ion with KBr, and three with K_2CO_3. In view of the possibilities of solid solution formation, it is remarkable that the

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[1] T. B. Douglas and J. L. Dever, *J. Research Natl. Bur. Standards*, **53**, 81 (1954).

[2] R. P. Seward, THIS JOURNAL, **64**, 1053 (1942).

TABLE I

THE LOWERING OF THE FREEZING POINT OF SODIUM HYDROXIDES BY VARIOUS SOLUTES

Solute Na_2CO_3					
N	0.00460	0.00912	0.0136	0.0199	0.0261
ΔT, °C.	1.8	4.6	7.1	10.0	12.8
i	0.85	1.10	1.13	1.09	1.07
Solute NaBr					
N	0.00765	0.0147	0.02520	0.0370	
ΔT, °C.	3.2	6.5	12.1	17.0	
i	0.93	0.96	1.00	1.00	
Solute KBr					
N	0.00282	0.00566	0.00924	0.0132	0.0178
ΔT, °C.	2.5	5.0	7.8	11.4	15.7
i	1.92	1.92	1.83	1.84	1.92
Solute K_2CO_3					
N	0.00515	0.00818	0.0110	0.0137	
ΔT, °C.	7.0	11.9	15.5	18.9	
i	2.95	3.17	3.07	3.00	

"i" factors come as close to whole numbers as they do.

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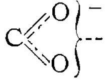
Infrared Absorption Spectra of Inorganic Coördination Complexes. IV. The Infrared Spectrum of Bis-(glycino)-zinc(II) Monohydrate[1a,b]

BY DANIEL M. SWEENY, COLUMBA CURRAN AND J. V. QUAGLIANO

RECEIVED JUNE 10, 1955

In the course of the investigation of metal amino acid complexes in progress in this Laboratory, the infrared spectrum of solid bis-(glycino)-zinc(II) monohydrate has been obtained. The spatial arrangement of ligands about the zinc ion has usually been considered to be tetrahedral,[2] corresponding to sp^3 hybridization of the bond orbitals. However, the X-ray investigations of Low[3] show conclusively that the glycine ligands are arranged in a planar fashion about the central zinc ion.

In a previous communication[4] it was postulated that the *trans* planar configuration of bis-(glycino)-copper(II) monohydrate complex is the result of an sp linear hybridization of copper bond orbitals. This explanation was based upon the observed infrared absorption spectrum of the copper(II) complex in the solid state. The spectrum was interpreted as indicating essentially covalent $N \rightarrow Cu^{++}$ bonds and essentially ionic  $C\begin{Bmatrix} O \\ O \end{Bmatrix}^{-}\text{---}Cu^{++}$ bonds in which the carboxylate ion resonance is preserved.

Experimental

Bis-(glycino)-zinc (II) monohydrate, $Zn(NH_2CH_2COO)_2 \cdot H_2O$ was prepared according to the method of Dubsky and Rabas.[5] The compound prepared in our laboratory was spectroscopically identical with a sample kindly supplied by Dr. Low.

Spectra were obtained from samples prepared in accordance with the KBr disk technique described previously.[6] The zinc complex gave very well-defined spectra similar to those reported for the Cu(II) and Ni(II) salts.[4] The frequencies in cm.$^{-1}$ observed for bis-(glycino)-zinc(II) monohydrate are as follows: 3450 (m), 3270 (m), 1603 (vs), 1447 (m), 1419 (m), 1404 (m), 1350 (w), 1314 (w), 1190 (w), 1146 (m), 1100 (m), 1060 (s), 954 (w), 907 (w), 719 (w). Abbreviations: m = medium, s = strong, w = weak, v = very.

Discussion

It is to be noted that absorption bands are observed at 3450 cm.$^{-1}$ (2.9 μ), 3270 cm.$^{-1}$ (3.06 μ) and 1603 cm.$^{-1}$ (6.24 μ) and no absorption band was observed in the region of 1720 cm.$^{-1}$ (5.8 μ). These regions are critical for the determination of the type of metal–ligand bonding present in amino acid–metal complexes.[4] The appearance of the NH stretching absorption maximum at 3270 cm.$^{-1}$, compared to the 3330 maximum in the spectrum of sodium glycinate, indicates the presence of $N \rightarrow Zn^{++}$ coördination. The absence of an absorption band near 1720 cm.$^{-1}$ (5.8 μ) and the presence of a very strong band at 1603 cm.$^{-1}$ (6.24 μ) indicate that the carboxyl to zinc bond has a high degree of ionic character.

These observations regarding the spectrum of bis-(glycino)-zinc(II) monohydrate are in accord with the evidence from X-ray diffraction of a square planar configuration for the zinc(II) complex. They indicate that linear sp metal bond orbitals are involved in the nitrogen-to-metal bonds in this complex as well as in the copper(II) and nickel(II) complexes previously reported. It is to be expected that all complexes of the type ZnX_2 in which X is a bidentate ligand having as one coördinating center a COO^- group forming essentially electrostatic $COO^- \text{---} Zn^{++}$ bonds, should have a *trans* square planar configuration if the other metal-to-ligand bonds are covalent. Further spectral studies on complexes of this type are being pursued in this Laboratory.

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(1) (a) Paper III in series, *J. Chem. Phys.*, in press. (b) Supported in part under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame.

(2) R. G. Dickinson, THIS JOURNAL, **44**, 774 (1922); C. H. MacGillavry and J. M. Bijvoet, *Z. Krist.*, **94**, 249 (1936).

(3) Private communication from Dr. Barbara Low, University Laboratory of Physical Chemistry Related to Medicine and Public Health, Harvard University.

(4) D. N. Sen, S. Mizushima, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 211 (1955).

(5) J. V. Dubsky and A. Rabas, Spisy vydávané privodovědeckou Fakultou Masarykovy Univ. No. 123, 3 (1930); *C. A.*, **25**, 2655 (1931).

(6) M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952); J. P. Faust and J. V. Quagliano, *ibid.*, **76**, 5346 (1954).