dides[6] and the tribromides[6b,7] were available from earlier investigations. Pure iodine bromide as well as samples of tetramethylammonium dibromoiodide (m.p. 192°), tetramethylammonium iodobromochloride (m.p. 204–205°) and tetramethylammonium tetraiodochloride (m.p. 108–109°) were kindly supplied by Dr. A. I. Popov and Mr. R. F. Swenson of this Laboratory.

Stock Solutions.—Homogeneous solutions of polyhalides or halogens in trifluoroacetic acid could be prepared only when the solute and solvent were shaken together long and vigorously. Often periods of shaking several hours in length were necessary. Particular care was taken to use tightly stoppered containers when handling the solutions in order to avoid halogen losses caused by volatility. A 5- or 10-ml. sample was mixed with at least 10 times its volume of water and the resulting aqueous solution was immediately subjected to an iodometric analysis for reducible halogen.

Absorption Spectra Measurements.—Measurements were carried out at 25° in calibrated silica cells of path length 1.00 ± 0.01 cm. with a Cary Model 11 recording spectrophotometer. The uniform nomenclature and symbology suggested by the National Bureau of Standards[8] have been used throughout this note.

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A Study of Alkaline Solutions of Zinc Oxide

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RECEIVED JUNE 9, 1954

In a recent paper[1] it was shown that in concentrated alkaline solutions dissolved zinc is present primarily as $Zn(OH)_4^{--}$. Since, however, claims have been made for the identification of a hydrogen zincate ion in such solutions[2-4] an attempt was made to verify this in dilute alkaline solutions where such ions are more likely to occur. This attempt involves the determination of the solubility of zinc oxide in alkaline solutions.

Since it was previously shown[1] that in strongly alkaline solutions $Zn(OH)_4^{--}$ was the highest hydroxyl containing species of dissolved zinc it can be assumed that all the dissolved zinc in dilute alkaline solutions will be in the form of ZnO or $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{--}$. Recently a claim has been made for the existence of $Zn(OH)_6^{-4}$ ions in alkaline solutions.[5] However, if the authors would have used the mean activity instead of the stoichiometric concentration of the hydroxyl ions in the Nernst equation, their results would have shown that $Zn(OH)_4^{--}$ is the highest hydroxyl containing zinc ion present.

If S represents the total solubility of zinc in such solutions, then

$$S = M_{Zn(OH)_2} + M_{Zn(OH)_3^-} + M_{(ZnOH)_4^{--}} \qquad (1)$$

Assuming the following equilibria

$$ZnO + OH^- + H_2O \longrightarrow Zn(OH)_3^- \qquad (2)$$

$$ZnO + 2OH^- + H_2O \longrightarrow Zn(OH)_4^{--} \qquad (3)$$

for which

$$K_1 = [M_{Zn(OH)_3^-} \times y_{Zn(OH)_3^-}]/[M_{OH^-} \times y_{OH^-} \times a_{H_2O}] \qquad (4)$$

$$K_2 = [M_{Zn(OH)_4^{--}} \times y_{Zn(OH)_4^{--}}][(M_{OH^-})^2 \times (y_{OH^-})^2 \times a_{H_2O}] \qquad (5)$$

then

$$S = M_{Zn(OH)_2} + [K_1 \times M_{OH^-} \times y_{OH^-}/y_{Zn(OH)_3^-}] + [K_2 \times (M_{OH^-})^2 \times (y_{OH^-})^2/y_{Zn(OH)_4^{--}}] \qquad (6)$$

The activity of water is omitted here since in dilute alkaline solutions this value approaches one. It may further be assumed that in a given solution the activity coefficients of all singly charged ions are the same. Equation 6 then becomes

$$S = M_{Zn(OH_2} + K_1 \times M_{OH^-} + K_2 \times (M_{OH^-})^2 \times (y_{OH^-})^2/y_{Zn(OH)_4^{--}} \qquad (7)$$

From the Debye–Hückel theory

$$\log y_{\pm(1-1)} = -A\sqrt{\mu}/(1 + Ba_1\sqrt{\mu})$$

$$\text{and } \log y_{\pm(1-2)} = -2A\sqrt{\mu}/(1 + Ba_1\sqrt{\mu})$$

where the numbers in parentheses refer to the type of ionic species present. From this it follows that

$$\log y_{\pm(1-2)} = 2 \log y_{\pm(1-1)} \qquad (8)$$

if $a_i(1 - 1) = a_i(1 - 2)$ which is a reasonable assumption for the systems studied here. From equation 8 it also follows that

$$y_{\pm(1-2)} = [y_{\pm(1-1)}]^2 \qquad (9)$$

The following series of relationships can then be made

$$\frac{(y_{OH^-})^2}{y_{Zn(OH)_4^{--}}} = \frac{(y+)^2(y_{OH^-})^2}{(y+)^2(y_{Zn(OH)_4})^{--}} = \frac{[y_{\pm(1-1}]^4}{[y_{\pm(1-2)}]^3} = \frac{[y_{\pm(1-1)}]^4}{[y_{\pm(1-1)}]^6} = \frac{1}{[y_{\pm(1-1)}]^2} \qquad (10)$$

Substituting this relationship in equation 7

$$S = M_{ZnO} + K_1 \times M_{OH^-} + K_2 \times (M_{OH^-})^2/[y_{\pm(1-1)}]^2 \qquad (11)$$

Although the Debye–Hückel equation holds only in dilute solutions still it is likely that a ratio of activity coefficients determined from this equation will hold up to somewhat higher ionic strengths.

Experimental

All solubilities were determined at 25 ± 0.1°. The best grade of powdered zinc oxide, potassium hydroxide and sodium hydroxide was used. The alkaline solutions were prepared by dilution of saturated solutions of potassium hydroxide and sodium hydroxide. Precautions were constantly taken to exclude carbon dioxide. The solutions were stored in polyethylene bottles and after zinc oxide was added the mixtures were kept in the constant temperature bath for a month. During this time they were shaken frequently. Finally they were carefully filtered using fritted glass filtering crucibles. The analysis for zinc was done amperometrically.[6] The mean activity coefficients of the hydroxyl ion were determined from the data given in the book of Harned and Owen.[7]

Results

Figure 1 gives a summary of the data obtained. It will be noted that the results for sodium hydroxide solutions are more erratic than those for potassium hydroxide. Extrapolation of these curves

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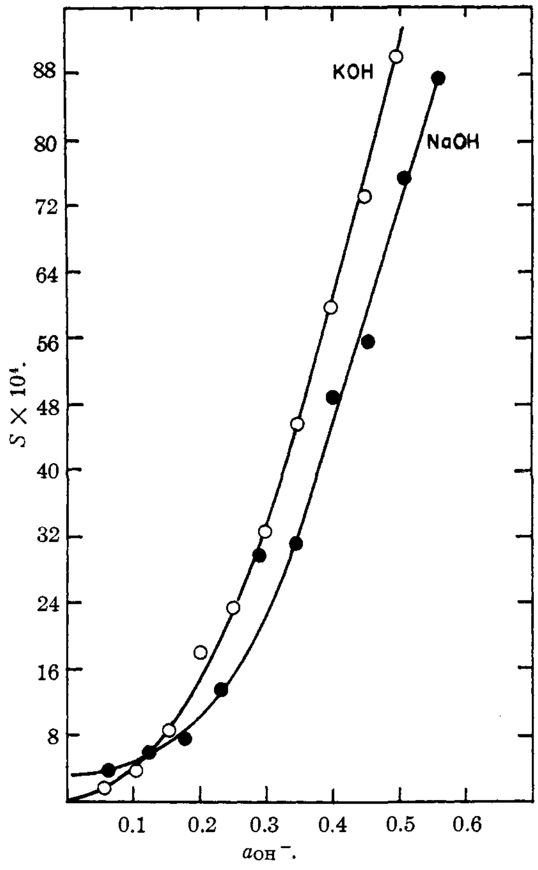

Fig. 1.—Solubility of zinc oxide in alkaline solutions.

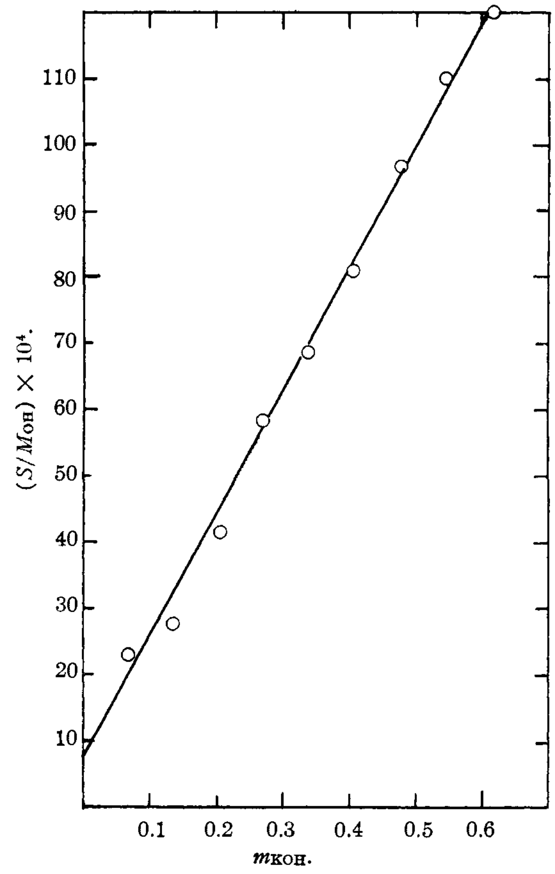

Fig. 2.—Plot to determine value of K_1.

shows that when the activity or molarity of the hydroxyl ion is zero, the value of the solubility in sodium hydroxide is 3×10^{-4} M while it is practically zero in potassium hydroxide solutions. According to equation 11 this then must be the value of the solubility of ZnO or $Zn(OH)_2$ in these solutions. The fact that there is some of this species in sodium hydroxide solutions may account for the irregularities in such solutions. It may also be related to the fact that in filtering some of the sodium hydroxide solutions it was difficult to obtain optically clear filtrates.

If for potassium hydroxide solutions $M_{ZnO} = 0$, then equation 11 may be rearranged to give

$$S/M_{OH^-} = K_1 + K_2 \times M_{OH^-}/[y_{\pm(1-1)}]^2 \quad (12)$$

Figure 2 shows a plot of S/M_{OH^-} *vs.* M_{OH^-} for potassium hydroxide solutions. Extrapolation of this to $M_{OH^-} = 0$ gives the value of 6×10^{-4}. This then is the value of K_1. Rearranging equation 12

$$(S/M_{OH^-} - K_1)[y_{\pm(1-1)}]^2/M_{OH^-} = K_2 \quad (13)$$

the value of K_2 can be calculated. The value obtained is $(100 \pm 2) \times 10^{-4}$. Using this value, ΔF°_{298} for reaction 2 is 2730 cal. From this and other accepted free energy values, $\Delta F^\circ_{Zn(OH)_4^{--}} = -205.2$ kcal./mole, in fair agreement with the value of -206.2 kcal. determined earlier.[1] Using 6×10^{-4} as the value of K_1, $\Delta F^\circ_{Zn(OH)_3^-}$ is -165.9 kcal./mole. On the basis of the values of K_1 and K_2 determined here, the distribution of $Zn(OH)_3$ and $Zn(OH)_4^{--}$ in alkaline solutions is shown on Fig. 3.

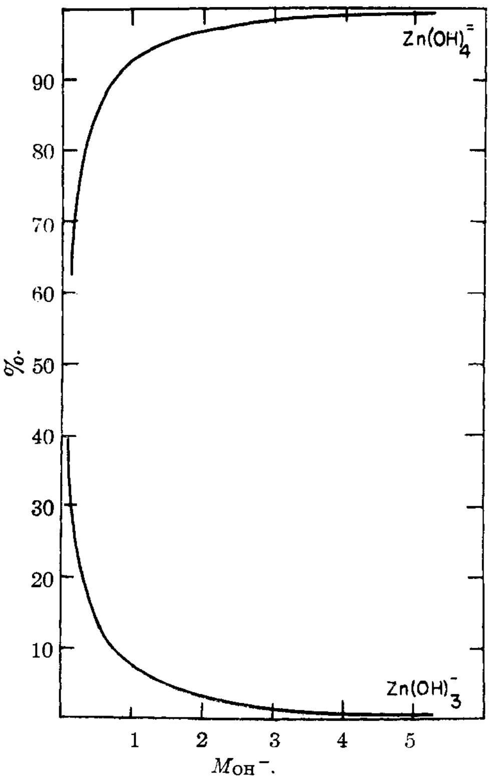

Fig. 3.—Distribution of zinc hydroxyl ions in alkaline solutions.

When the solubility values of zinc oxide in sodium hydroxide solutions are treated in the same way as described above for potassium hydroxide solutions, the values of K_1 and K_2 turn out to be 6×10^{-4} and 6×10^{-3}, respectively. However, due to the erratic nature of these results the precision is not great and the corresponding values determined from potassium hydroxide solutions are considered more reliable.

Recently a report on the dissociation constants of zinc hydroxide has appeared.[8] The two types of zinc ions are given as $HZnO_2^-$ and $ZnO_2^{=}$. However, using the dissociation constants given by these authors and assuming that the zinc ions are $Zn(OH)_3^-$ and $Zn(OH)_4^{=}$, the values for the free energy of formation of these ions are calculated to be −166.3 kcal./mole and −205.6 kcal./mole, respectively. This is in fair agreement with the values of −165.9 and −205.2 kcal./mole calculated from the formation constants determined by our solubility measurements.

Acknowledgment.—The work reported here was supported by a grant from the Research Corporation.

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Solvents Having High Dielectric Constants. I. Conductimetric Studies of Solutions of Hydrogen Chloride and Potassium Chloride in Formamide[1]

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RECEIVED JULY 2, 1954

This paper describes the first of a series of studies of the properties of solvents having dielectric constants greater than that of water. These are being used either as pure substances or mixed with another more or less familiar solvent having a lower dielectric constant. Several phases of these studies have been completed and will be reported in later papers; others are in progress.

Cryoscopic data[2] which were used to calculate the apparent degrees of dissociation of certain salts and acids in formamide at higher concentrations, and spectrophotometric studies of cobalt chloride[3] in this solvent, have been reported from this Laboratory. Values for the dielectric constant of formamide over the temperature range 15 to 35° have been determined here.[4] Despite the numerous difficulties encountered in the preparation and preservation of good quality formamide, it is believed that these data are accurate to within 0.4%.

In another paper[5] certain N-substituted amides have been described. These were found to have very high dielectric constants, some even approaching 200 at room temperature. Later work has shown that these liquids are good solvents for several inorganic salts. Our program includes numerous studies of these N-substituted compounds.

Experimental

Apparatus.—The bridge assembly has been described in a previous paper.[6] Three Washburn-type cells with lightly platinized electrodes, having constants ranging from 0.07292 to 2.2167, were used. The constants were determined by the method of Jones and Bradshaw.[7] No significant change in the cell constants could be detected over the temperature range for which they were used. The cells were held in a thermostated oil-bath which maintained a constant temperature to within ±0.02°.

Solvent.—The best obtainable commercial grade of formamide was purified by several distillations over calcium oxide at a pressure <0.1 mm. where the temperature remained between 51 and 58°. Decomposition of the vapor was held to a minimum by using a fractionating column in which the distillate vapors were carried over a short path and condensed immediately to room temperature. As a result of using a Glas-Col heating mantle and low pressure, distillation proceeded from surface evaporation and bumping was eliminated. The resulting solvent showed specific conductances ranging from 1×10^{-5} to 3×10^{-5} ohm^{-1} cm.$^{-1}$ at 20°.

Electrolytes.—Reagent grade potassium chloride was recrystallized and fused. Anhydrous hydrogen chloride was prepared by dropping concentrated sulfuric acid into concentrated hydrochloric acid and passing the resulting vapor through drying towers containing concentrated sulfuric acid.

Solutions.—Solutions were prepared and dilutions made on a weight basis. All transfers were made in a dry atmosphere.

TABLE I

PROPERTIES OF FORMAMIDE

Temp., °C.	Density, g./ml.	Viscosity, poise	Dielectric constant
3	1.1474	0.0654	118.3
5	1.1458	.0618	117.5
20	1.1332	.0385	111.5
40	1.1161	.0237	103.5

Results and Discussion

All conductances were corrected by subtracting the conductance of the solvent from that of the solution. Λ_0 values were obtained by empirical extrapolation of plots of Λ *vs.* $\sqrt{C}$. Although there is some uncertainty in the values of the limiting equivalent conductances, they are believed to be accurate to within 1 or 2%. Slopes of the limiting tangents were calculated by the limiting Onsager[8] equation in which most recent values[9] for the physical constants were used.

No conductance data for HCl in formamide have been found in the literature. Our values for solutions of KCl in this solvent, translated into data for 25°, are about 4% higher than those reported by Davis and Putnam.[10] The higher viscosity and larger dielectric constant of our solvent are evidences of its greater purity.

Plots of Λ *vs.* $\sqrt{C}$ for these solutions resemble those for the same electrolytes in water in that they approach the theoretical limiting slope from above. This may be interpreted as indicating practically complete absence of ion association. Correspond-

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