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 $\mathrm{HZnO_2^-}$ and $\mathrm{ZnO_2^{=}}$. However, using the dissociation constants given by these authors and assuming that the zinc ions are $\mathrm{Zn(OH)_3^-}$ and $\mathrm{Zn(OH)_4^{=}}$, 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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TABLE II

CONDUCTANCES OF SOLUTIONS OF HYDROGEN CHLORIDE AND POTASSIUM CHLORIDE IN FORMAMIDE

3°		20°		40°	
		Hydrogen chloride			
C ($\times 10^2$)	Λ	C ($\times 10^2$)	Λ	C ($\times 10^2$)	Λ
0.00	(14.41)	0.00	(24.50)	0.00	(39.40)
4.84	12.39	5.38	21.20	3.28	35.24
6.56	12.07	6.42	21.00	8.04	32.93
13.13	11.42	7.35	20.82	9.79	32.38
26.25	9.99	8.67	20.60	37.15	27.32
52.50	8.40	10.09	20.28	52.51	25.10
		11.77	19.98		
		13.83	19.57		
		15.89	19.21		
		29.93	17.45		
		45.53	15.82		
Theoretical slopes					
8.97		15.23		24.86	
		Potassium chloride			
0.00	(16.94)	0.00	(26.38)	0.00	(41.66)
0.52	16.13	0.52	25.31	0.51	40.05
1.04	15.86	1.03	24.81	1.01	39.35
2.60	15.49	2.57	24.22	2.53	38.36
16.13	13.26	15.95	20.87	15.71	33.06
36.40	11.64	36.00	18.42	35.46	29.30
70.78	9.54	70.00	15.33	68.94	24.62
Theoretical slopes					
9.72		15.49		25.18	

ence with the theoretical to nearly 0.01 N, which is shown in these graphs, is unexpected in view of the fact that 0.003 N is the upper limit for similar behavior by the same solutes in water. Furthermore, the difference between these types of solutions becomes much greater if the concentrations are thought of in terms of relative numbers of molecules rather than molarity.

The Kohlrausch plots exhibit much less upward concavity with increased concentration than for these solutes in aqueous solutions; at higher concentrations they tend to approach linearity. This behavior may be produced by an inflection resulting primarily from viscosity effects.

The Walden products for the HCl system at 3, 20 and 40° are 0.942, 0.943 and 0.932. For the KCl system at 5, 20 and 40°, these values are 1.047, 1.016 and 0.987. The conductance-viscosity product for KCl in formamide is markedly less than it is in water (1.34 at 25°) and greater than it is in most organic solvents.

The lower limiting conductance of HCl is evidence that the solvated proton is larger, hence less mobile, than the solvated potassium ion. In addition, the absence of abnormally high cation conductance in the acid solution is proof that the proton does not move through this solvent by some unique mechanism as it does in water. A similar conclusion has been drawn from studies of acids in amine solvents[11] and in dimethylformamide.[12]

Acknowledgment.—The authors gratefully acknowledge the assistance and advice given by Drs. Paul G. Sears and Charles E. Holley in connection with this work.

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Inorganic Complex Compounds Containing Polydentate Groups. X. Zirconium(IV) Complexes

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RECEIVED AUGUST 9, 1954

This study[2] was designed to explore by spectrophotometric means the formation of complex ions of zirconium(IV) with the bidentate coördination agent, 1-nitroso-2-naphthol and *o,o'*-dihydroxyazobenzene, a possible tridentate group. A consideration of the structural formula of the latter indicates that coördination to the two hydroxy and the azo groups may be possible.

Experimental

A. **Reagents.**—Zirconium tetrachloride, $ZrCl_4 \cdot 8H_2O$, obtained from the Fairmount Chemical Company was recrystallized six times from concentrated HCl solutions.

The 1-nitroso-2-naphthol, practical grade (melting point 109°), was obtained from the Eastman Kodak Company. This material was dissolved in ethanol and recrystallized with water.

The *o,o'*-dihydroxyazobenzene was prepared by the method of Weselsky and Benedict[3] as modified by Willstätter.[4]

Recrystallization from methyl alcohol produced a golden-yellow product melting at 172° (reported 171–173°). The other reagents were C.P. grade chemicals.

B. **Instruments.**—The Beckman Model G *p*H meter was used in the determination and adjustment of the *p*H of the solutions throughout this study.

All spectrophotometric determinations were made on the Beckman model DU spectrophotometer. Matched ten millimeter Corex cells were used for measurements in the visible range. Matched ten millimeter quartz cells were used with the ultraviolet attachment for measurements in this region of the spectrum.

C. **Spectrophotometric Investigations.** 1. **1-Nitroso-2-naphthol Complexes.**—The absorption spectrum of the zirconium(IV) 1-nitroso-2-naphthol complex was determined using a 50% ethanol solution which was 5×10^{-4} M in 1-nitroso-2-naphthol and 5×10^{-4} M in $ZrOCl_2$. The solution was 1×10^{-1} M in $NaNO_3$ as inert electrolyte. The solution was adjusted to *p*H of 3.5 by the addition of small amounts of M HNO_3.

Continuous variation and saturation studies[5] were made at 480 mμ on a series of a similar solution.

2. ***o,o'*-Dihydroxyazobenzene Complexes.**—The absorption spectrum of a 50% ethanol solution 1.5×10^{-4} M in *o,o'*-dihydroxyazobenzene and in $ZrOCl_2$ was determined from 250 to 600 mμ. An inert electrolyte concentration in $NaClO_4$ was maintained at 3×10^{-2} M. The solution was allowed to stand for 40–48 hours to reach equilibrium. Nitrogen was bubbled through the solution before and after mixing.

Continuous variation and saturation studies were made on similar solutions.

A. Studies of Zirconium(IV) with 1-Nitroso-2-naphthol. 1. Spectral Studies.—Figure 1 shows that the regions from 450 to 500 mμ and 270 to 300 mμ are best suited for continuous variation studies.

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