Discussion

It is strange to find that with $FeCl_3$ the molecular weight increases with a diminution in the concentration of the solute. Similar results were also noticed by Kahlenberg and Lincoln.[4] The molecular weight obtained for the compound $FeCl_3 \cdot POCl_3$ is 344, while the calculated value is 316. The difference between the observed molecular weight (310) and the calculated value (785.5) for the compound $2FeCl_3 \cdot 3POCl_3$ is quite considerable. This may be due to the dissociation of the complex.

$$2FeCl_3 \cdot 3POCl_3 \rightleftarrows 2(FeCl_3 \cdot POCl_3) + POCl_3 \quad (1)$$

This also explains the equality in conductivity of the two complexes for a given concentration of ferric chloride.

Table III indicates that the specific conductivity of the complex $FeCl_3 \cdot POCl_3$ is invariably higher than the sum of the conductivities of the individual components. This increase in the conductivity can be explained by assuming the dissociation of the complex as

$$FeCl_3 \cdot POCl_3 \rightleftarrows FeCl_4^- + POCl_2^+ \quad (2)$$

The studies described above indicate the formation of the two complexes $2FeCl_3 \cdot 3POCl_3$ and $FeCl_3 \cdot POCl_3$. The existence of the compound $2FeCl_3 \cdot POCl_3$ reported in the literature, however, could not be confirmed.

Acknowledgment.—The authors wish to thank Prof. K. R. Krishnaswami, Head of the Department of General Chemistry, Indian Institute of Science, Bangalore, for his keen interest and helpful criticism during the progress of this investigation.

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An Aqueous Synthesis of Barium Titanate

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RECEIVED JANUARY 12, 1955

High temperature calcination and reaction of titanium dioxide and barium as the oxide, nitrate, carbonate or hydroxide, or as the mixed oxalates are the usual bases for the preparation of barium titanate ($BaTiO_3$). In the method reported herein crystalline barium titanate as well as various titanate solid solutions are synthesized directly from aqueous solution. This method is based upon the precipitation of barium titanate upon addition of a titanium ester to an aqueous solution of a soluble barium salt. Analogous to the solution chemistry of the zirconates, vanadates and chromates, a strongly alkaline environment is found to be essential for the formation of the "meta" salt. Precipitation from neutral and acid solutions result in the formation of hydrated titanium dioxide only.

In this method a dilute propyl alcohol solution of a titanium ester such as tetrapropyltitanate or an ester of a higher alcohol is added dropwise and with vigorous stirring to a degassed water solution of barium hydroxide, *p*H 11 to 14. Reaction in a KOH solution is used where a controlled *p*H is desirable. No chemical or physical differences in the nature of the product could be detected by reaction in the presence of potassium ion or as a function of the *p*H over this range. Sufficient excess of the ester is added to result in a final 1:1 or greater molar ratio of BaO to TiO_2. A white, fine grained (1 to 5 μ), homogeneous phase readily precipitates on mixing over the temperature range 20 to 100°. Reaction above 80° yields a crystalline product directly. The low temperature precipitate must be aged for from one to two hours at the boiling point. The precipitate is filtered and then washed with hot, degassed distilled water to remove excess barium salt.

The X-ray diffraction pattern of the product is identical to that characteristic of the tetragonal modification of $BaTiO_3$ as synthesized by means of high temperature solid state reaction. This method has also been used successfully for the introduction of trace impurities and for the synthesis of homogeneous solid solutions in which partial substitution has been made for the barium ion.

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Basicity of the Amide Bond[1,2]

BY A. R. GOLDFARB, A. MELE AND N. GUTSTEIN

RECEIVED JULY 6, 1955

During the course of an investigation of the ultraviolet absorption spectra of amides and peptides it was observed that these compounds showed a marked lowering of the molar extinction coefficient (ϵ) in concentrated sulfuric acid solutions. The shape of the curves, ϵ *vs.* concentration of sulfuric acid, suggested that we were measuring the proton binding ability of the amide and peptide structures. Cryoscopic measurements[3,4] in 100% H_2SO_4 have indicated that amides and carboxylic acids bind one proton. Hall[5] using potentiometric methods, measured the acid dissociation constant for the acetamidonium ion and found pK_a[6] values of −0.5 in water and −1.65 in glacial acetic acid. More recently Lemaire and Lucas[7] determined the thermodynamic pK_a values of a number of weak bases, including acetamide, by use of an indicator method. The value of pK_a determined in the last instance was about −0.04. We have made a study of a series of acetamide derivatives, using a spectrophotometric method, to determine the effect of substituent on the nitrogen and of adjacent charge on the basicity of the amide bond.

Experimental

Materials.—Acetic acid, acetamide, methyl- and dimethylacetamide, glycinamide and acetylglycine were commercially available materials which were purified by fractional distillation or crystallization. The butylacetamides were prepared by mixing acetic anhydride (2 moles) with the

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[1] Supported by Grant #NSF-G617 from the National Science Foundation.

[2] Reported, in part, at the Meeting of the American Chemical Society held in New York during March of 1954.

[3] A. Hantzsch, *Ber.*, **64**, 667 (1931).

[4] J. L. O'Brien and C. J. Niemann, THIS JOURNAL, **72**, 5348 (1950).

[5] N. F. Hall, *ibid.*, **52**, 5115 (1930).

[6] $pK_a = -\log K_a$, K_a = (acetamide)(H+)/(acetamide H+).

[7] H. Lemaire and H. J. Lucas, THIS JOURNAL, **73**, 5198 (1951).