sodium hydroxide solution and distilled; 37 g. of a mixture of starting material and the corresponding ketone was obtained. Acidification of the sodium hydroxide extract caused the precipitation of 7.6 g. of *p*-toluylvaleric acid, m. p. 152.5–154°[9] after recrystallization from a benzene-ethanol mixture; neutralization equivalent, 223 (calcd., 220). δ-Benzoylvaleric acid has been obtained from 2-phenylcyclohexanol under similar conditions.[3]

**2-Alkoxycyclohexanols.**—In a typical experiment, 2-amyloxycyclohexanol was prepared by refluxing for twenty-two hours a solution of 49 g. of cyclohexene oxide[8] in 200 ml. of *n*-amyl alcohol containing 0.5 g. of dissolved sodium. The reaction mixture was distilled and 72 g. (77%) of 2-amyloxycyclohexanol was collected at 100–113° (11 mm.). When alcohols boiling above 200° were used, the solutions were heated at 180–200°.

In the reaction between 35 g. of cyclohexene oxide and 140 ml. of phenethyl alcohol, the first portion of 2-(β-phenethoxy)-cyclohexanol collected on distillation contained *trans*-1,2-cyclohexanediol, 4 g. of which crystallized out on cooling the mixture. It was recrystallized from hexane and identified by its melting point (102–103°),[10a] dibenzoate melting point (91.5–92°),[10b] and composition.

*Anal.* Calcd. for $C_6H_{12}O_2$: C, 62.0; H, 10.4. Found: C, 62.1; H, 10.4.

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[9] Brosche, *Ber.*, **52**, 2080 (1919), reports a melting point of 153–154°.

[10] (a) Verkade, Coops, Maan and Verkade-Sandbergen, *Ann.*, **467**, 217 (1928); (b) **477**, 289 (1930).

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## The Solubility of Aminoguanidonium Bisulfate in Water and in Sulfuric Acid Solutions[1]

BY JOHN J. PITHA[2] AND G. B. L. SMITH[3]

In the reduction of nitroguanidine in a sulfuric acid solution, the end-product of the reaction is aminoguanidonium bisulfate. In order better to control the recovery of this salt, some investigations were made into the solubility of aminoguanidonium bisulfate in water and in solutions of various sulfuric acid concentrations.

### Experimental

The solubility of aminoguanidonium bisulfate was determined by preparing a saturated solution of the salt in the appropriate solvent at a definite temperature. After equilibrium had been established, a sample of the solution was withdrawn and transferred to a tared volumetric flask and weighed. This solution was then diluted to volume and analyzed for aminoguanidine by the method of Smith and Wheat.[4]

These studies were carried out in a specially constructed three-necked flask of 100 ml. capacity. One neck was used to insert a thermometer into the solution, one neck allowed the entry of an all-glass stirrer, and the third neck was used as an addition port. Ground glass joints were used throughout. Solution temperatures from 5 to 40° were measured with an unjacketed thermometer, but higher temperatures were measured with a thermometer suspended within a glass jacket. The bulb of the flask and the lower third of the necks were immersed in a 7.5-gal. water-bath. This thermostat was equipped with both heating and cooling coils and the temperature of the solution in the reaction flask was controlled to ±0.03°.

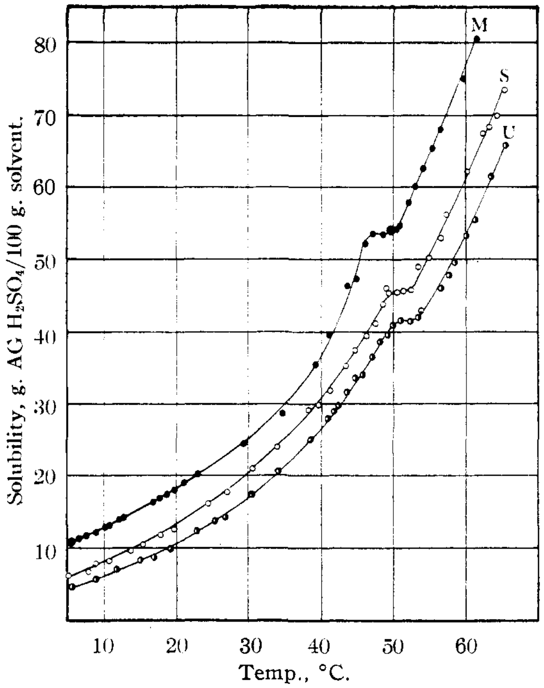

Fig. 1.—M, ●, $H_2O$; S, ○, 0.7419 *N* $H_2SO_4$; U, ◑, 1.4088 *N* $H_2SO_4$.

Saturated solutions of the salt at a particular temperature were prepared by adding an excess of the solute to the solvent and stirring the solution until equilibrium had been established. The attainment of equilibrium was proven by successive sampling and analysis at regular intervals of time until three successive values were in agreement. A half-hour lapse of time after the solution had come to temperature was usually sufficient for equilibrium to be reached. In certain portions of these studies, the equilibrium was approached from both directions in order to establish definitely the values reported.

In order to avoid errors that might occur in the removal and transfer of samples due to crystallization of the salt from the saturated solution while in the sampling tube, pipets used for this purpose were kept in an oven and were used warm. The operation was performed with sufficient speed that no difficulty with crystallization was encountered.

At least three determinations of solubility were made at each temperature, and in the cases where abnormalities were observed sufficient determinations were made to establish the points reported. The accuracy of the analytical procedure was such that an error of 0.1% was average. Precision of results on duplicate sets of samples was of the order of 1 part in 1000 parts. The solubility of aminoguanidonium bisulfate in water, 0.7419 *N* sulfuric acid and 1:4088 *N* sulfuric acid was determined. The results of the solubility determinations are summarized in Fig. 1. Crystals obtained by evaporation at temperatures above and below the inflection temperatures in all cases analyzed 99.5% or better for aminoguanidonium bisulfate, and macro observations of these crystals showed no differences in crystalline form. The nature of the inflection observed in each of the curves is not completely understood, but additional information is being sought and will be reported in a subsequent paper.

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[4] Smith and Wheat, *Ind. Eng. Chem., Anal. Ed.*, **11**, 200 (1939).