with water with agitation in a thermostat. The results are given in Table I.

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The Titration of Polyamines in the Presence of Sodium Dodecyl Sulfate[1]

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In studies of competitive equilibria between proteins and polyamines for metal ions, it became necessary to evaluate the purity of a number of these polybases. For this purpose, the titration procedure of Gause, Crumpler and Jonassen[2] was followed. In essence their method consists of plotting the derivative of the titration curve, $\Delta(p\mathrm{H})/\Delta V$, against V, the volume of added standard acid, and observing whether the peaks occur at the proper mole ratios. With tetraethylenepentamine, for example, these investigators[2] felt that end-points for four of the five protons taken up by the base could be observed readily.

In our experience we felt very uncertain about the exact position of most of the end-points. Since a small error in this reading becomes greatly magnified in calculations of per cent. purity, we searched about for a method of sharpening the titration curve.

A suitable method suggests itself on consideration of the fundamental reason for the shallow slopes in the titration curve in the first place. Ordinarily the pK_a of an amine in aqueous solution lies near 10 so that titration with nitric acid gives a sharp end-point. With several basic nitrogen groups on the same molecule, however, each added proton magnifies the electrostatic repulsion toward subsequent protons and hence pK_a's are lowered greatly. To overcome this electrostatic repulsion, it seemed appropriate therefore to add a large organic anion to the solution so that as the polyammonium ion is formed, repulsion of successive protons would be minimized by formation of an anion-cation complex.

In practice sodium dodecyl sulfate proved to be eminently suitable. Titration curves were greatly sharpened with triethylenetetramine,[3] tetraethylenepentamine and the hexamine[3] N,N,N',N'-(β-aminoethyl)-ethylenediamine, respectively (Fig. 1). It seems, therefore, that this procedure should be applicable generally in examinations of the stoichiometry of acid titrations of polyamines.

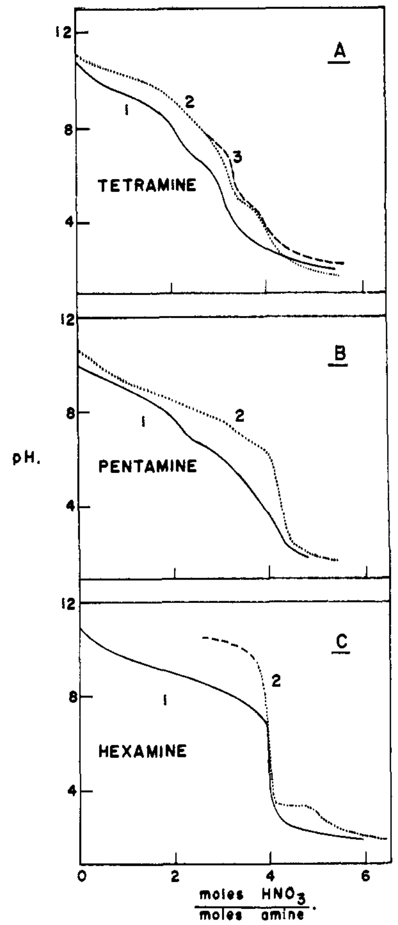

Fig. 1.—A, titration of triethylenetetramine in aqueous solution: 1, 0.198×10^{-3} mole tetramine in water; 2, 0.198×10^{-3} mole tetramine with 2.06×10^{-3} mole sodium dodecyl sulfate (U.S.P.); 3, 0.111×10^{-3} mole tetramine with 2.24×10^{-3} mole sodium dodecyl sulfate (crystalline) (curves 1 and 2 in nitrogen atmosphere).

B, titration of tetraethylenepentamine: 1, 0.335×10^{-3} mole pentamine; 2, 0.335×10^{-3} mole pentamine with 1.66×10^{-3} mole sodium dodecyl sulfate (crystalline).

C, titration of N,N,N',N'-(β-aminoethyl)-ethylenediamine (hexamine): 1, 0.129×10^{-3} mole hexamine; 2, 0.129×10^{-3} mole hexamine with 0.878×10^{-3} mole sodium dodecyl sulfate (crystalline).

Experimental

A commercial grade of triethylenetetramine was used as received. Tetraethylenepentamine was fractionated by the ion exchange method of Gause, Crumpler and Jonassen.[2] The hexamine, N,N,N',N'-(β-aminoethyl)-ethylenediamine was a research sample of high purity.[6] Purified sodium dodecyl sulfate was a product of E. I. du Pont de Nemours and Company. A U.S.P. grade of sodium dodecyl sulfate also was used.

Titrations were carried out with a Beckman Model G pH meter using external electrodes. Triethylenetetramine was titrated in an atmosphere of nitrogen as well as in air.

In each titration with dodecyl sulfate an insoluble anion-cation complex was formed ultimately. The formation of this complex produced drifts upward in pH, probably due to slow diffusion of protons into the insoluble complex. Continuous stirring resulted in reproducible readings.

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[2] E. H. Gause, T. B. Crumpler and H. B. Jonassen, THIS JOURNAL, **73**, 5457 (1951).

[3] Only in the presence of dodecyl sulfate could the uptake of the fourth proton by triethylenetetramine, and of the fifth proton by hexamine, be observed distinctly. Pentamine evidently does not form a pentammonium complex and hexamine does not form a hexammonium complex.[4]

[4] G. Schwarzenbach and P. Moser, *Helv. Chim. Acta*, **36**, 581 (1953).

[6] We are indebted to Dr. W. Gauss of the Leverkusen Works of I. G. Farbenindustrie for a gift of this material.