

uring the viscosity of a 3.6% sucrose solution at 25°, taking the figures given by Gosting and Morris<sup>5</sup> as standard. Kinetic energy corrections were found to be negligible.

The junior author is indebted to the University of Western Australia for a Hackett Scholarship during the tenure of which this work was done.

(5) L. J. Gosting and M. W. Morris, *THIS JOURNAL*, **71**, 1993 (1949).

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### Purification of Tetraethylenepentamine

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Tetraethylenepentamine,  $\text{NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$ , has recently become of importance as a colorimetric reagent<sup>1</sup> and as an activator in low temperature copolymerization.<sup>2</sup> However, in both these instances relatively impure pentamine was used. The peculiar form of the graph obtained by Crumpler<sup>1</sup> depicting the effect of excess pentamine on color development with  $\text{Cu}^{++}$  ion suggested the need for a study of the complexes existing in solution. The purified sample is being used for a continuous variations study. Spolsky and Williams<sup>3</sup> noted the presence of iron in their pentamine samples and suggested the desirability of a study to differentiate the functions of iron and pentamine in the activator effect.

Previous attempts in this Laboratory to isolate this amine by fractional distillation and by the selective precipitation of normal as well as acid salts of various anions were unsuccessful. We have now succeeded by an ion exchange method in separating pure pentamine from the commercially available material which contains lower and higher molecular weight polyamines as well as an appreciable amount of iron.

Further work is in progress to determine the structure and stabilities of the complexes formed between the various metal ions and pentamine similar to that with the lower amines.<sup>4</sup>

#### Experimental

An ion exchange column 90 cm. in length and 2.2 cm. in diameter, containing the acid form of 250-500 mesh Ion-X (Dowex-50) resin was prepared. A thick slurry of the resin in distilled water was poured into the column which was partially filled with water and the resin bed was allowed to settle. A liter of solution of commercial tetraethylenepentamine (40 g./l.) was decolorized with Norit and passed through the column under about 300 mm. pressure. The amines were absorbed on approximately  $\frac{1}{3}$  of the column. The column was then washed with distilled water and eluted with 0.25 *N* NaOH. The flow-rate was 0.7 cc./min. The passage of the amine layer down the column can be followed readily because of the difference in color of the several forms of the resin. The amine solution was collected in 50-cc. fractions. The eluted amine was slightly discolored; therefore, alternate fractions were decolorized with 0.5 g. of Norit and a 25-ml. aliquot diluted with 100 cc. of water, saturated with  $\text{HNO}_3$ , and titrated potentiometri-

cally with 0.5 *N*  $\text{HNO}_3$ . Standard HCl and KCl, supporting electrolyte, may also be used. Fractions 5, 7, 9 and 11 were mainly tetraethylenepentamine together with some impurities.

The combined pentamine fractions, together with their even-numbered counterparts (250 cc.) were treated with Norit. They were then passed through a column (29 × 1.7 cm.) operated by an aspirator, at a flow-rate of 0.9 cc./min. and eluted with 0.25 *N* NaOH as described above. Again 50-cc. fractions were collected and 10-ml. aliquots titrated with 0.2 *N*  $\text{HNO}_3$  with  $\text{KNO}_3$  as supporting electrolyte. The following yield was obtained. (1) Fractions 1 and 2 were pure pentamine solution; (2) fraction 3 was 95% pure pentamine solution; and (3) fraction 4 was a highly impure mixture.

In order to eliminate discoloration which was probably the result of decomposition encountered using the acid form of the resin, attempts were made to adsorb the amine on both the sodium and potassium resins, but in the concentrations used in this work, the aminium ions would not replace the alkali metal ions.

It is important that the resin bed be kept in contact with liquid at all times. If allowed to run dry, channeling will occur, permitting mixing of the NaOH and amine solutions. Should this occur, the  $\text{Na}^+$  ions may be removed by passing the solution over a small resin bed, the amount of resin depending on the amount of  $\text{Na}^+$  present.

The iron normally present in the commercial tetraethylenepentamine is also removed during the purification. In basic solution the iron-amine complex is strongly adsorbed on the resin, and on reconversion of the resin, is displaced by the acid. Below a pH of about 3, the complex is red, and above this pH it is yellow. Both basic and acidic solutions of the complex were tested for Fe with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . The acid solution gave a positive test indicating greater stability of the basic yellow form. Some of the complex was oxidized to  $\text{Fe}^{+++}$  and gave a positive test with KCNS. The eluted amine solution was found to be free of iron by these tests.

The purity of each sample was determined from the titration. The simple titration graph is not satisfactory since only the final inflection point is sharp enough to be accurately located on the curve. The differential plot ( $\Delta\text{pH}/\Delta V$  vs.  $V$ ) shows that there are breaks corresponding to the neutralization of the fourth and fifth nitrogen atoms of the molecule with indications of breaks for the second and third. The coincidence in the position of the maxima with their theoretical location is taken as the indication of purity (see Fig. 1).

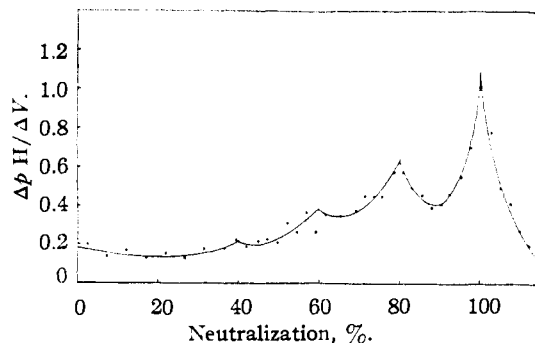


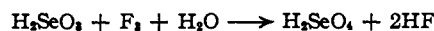
Fig. 1.

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### The Fluorination of Aqueous Selenious Acid

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Selenious acid solutions of varying strengths have been fluorinated in an attempt to determine optimum conditions for conversion to selenic acid.



(1) T. B. Crumpler, *Anal. Chem.*, **19**, 325 (1947).

(2) R. Spolsky and H. L. Williams, *Ind. Eng. Chem.*, **42**, 1847 (1950).

(3) Private communication, H. L. Williams to H. B. Jonassen.

(4) H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, *THIS JOURNAL*, **73**, 4968 (1950).