The Determination of Unreacted Amines in Long Chain Amine Oxides by Potentiometric Titration

C.N. WANG and **L.D. METCALFE**, Akzo Chemie America Research Laboratories,
8401 W. 47th Street, McCook, IL 60525

ABSTRACT

During the manufacture of amine oxides information on the amount of unreacted tertiary amine present is needed in order to follow the reaction. A number of analytical procedures have been devised to obtain this information. Wet methods include redox titrations of the amine oxide and differential titrations using derivatization of the amine or amine oxide. Various chromatographic procedures using GC, TLC and HPLC also have been reported. All of these procedures have some limitations. A simple, rapid, quality control procedure would be useful. A rapid, nonaqueous titration procedure has been developed in our laboratory that makes use of the "anomalous salt" behavior of amine oxides. A modified solvent and titrant is used to obtain two potential breaks in the titration. The first break corresponds to half of the amine oxide. The second break represents the second half of the amine oxide plus any unreacted amine. With this information the amine oxide and unreacted amines can be calculated. The precision and accuracy of the titration have been studied using samples spiked with known amounts of amine.

INTRODUCTION

Long chain amine oxides are most interesting compounds. The amine oxides have found increasing use in many industrial and consumer product applications. This includes use as surfactants, antimicrobial agents and emulsifiers. The amine oxides are made by oxidation of tertiary amines, usually with hydrogen peroxide. They resemble amines in basicity. However, they also exhibit some of the properties of quaternary ammonium compounds such as increased water solubility.

The main analytical quality control problem of amine oxides is the determination of the precursor free amine in the presence of amine oxide. Though the analytical literature for amine oxides is not very large, it is quite varied in methodology approaches. Reduction methods using stannous chloride (1), titanous chloride (2,3) and iodine (4) have been described. A number of nonaqueous acid titration procedures have been published (5-8). Chromatographic methods also have been described for this analysis which includes TLC (9-11) and GC (12). Polarography also has been used to determine amine oxides (13).

A simple, nonaqueous titration procedure for amine oxides which would give both amine oxide and free amine would be valuable for quality control. Bezinger (8) indicated that amine oxides and other amines can be titrated potentiometrically in a differentiating nonaqueous solvent. He observed two potential breaks when titrating amine oxides. He claimed that N-oxides are titrated in two stages because they form "anomalous" salts in which two molecules of base are required for one molecule of acid. The titration scheme is shown as follows:

1st stage:

$$2\,R{-}(CH_3)_2{-}N \rightarrow O + HA \rightarrow$$

$$[R{-}(CH_3)_2{-}N{-}O\cdots H\cdots O{-}N{-}(CH_3)_2{-}R]^+A^-$$

2nd stage:

$$[R{-}(CH_3)_2{-}N{-}O\cdots H\cdots O{-}N{-}(CH_3)_2{-}R]^+A^- + HA$$

$$\rightarrow 2\,[R{-}(CH_3)_2{-}N{-}OH^+A^-]$$

Anomalous salts of this type have been observed in aromatic heterocyclic base N-oxides (14,15); little work has been done on aliphatic amine oxides in mixtures with the starting amine to verify Bezinger's work. In our procedure, modified solvent and titrant system was developed that was used to establish a quantitative method for long chain amine oxides and the precursor amine in mixtures. Some differences from Bezinger's work were observed. It was found that the method can be applied only to aliphatic amine oxides that have a N-methyl stucture. Two inflection points were observed in the potentiometric titration curve when the amine oxides were titrated. The first inflection point was found to occur when half of the N-oxides had been titrated. The second inflection point was found to be due to the rest of the N-oxides plus any unreacted free amine present.

EXPERIMENTAL

Reagents were 0.1 N perchloric acid in acetonitrile, standardized with Tris-(hydroxymethyl) aminomethane in acetic acid; methyl ethyl ketone, ACS grade, and acetonitrile, ACS grade. Any automatic titrator or pH meter with a glass-platinum electrode system can be used. The platinum electrode works best imbedded in the titrant stream (Fig. 1). A sample containing about 1.5 milliequivalents/g of long chain amine oxide is dissolved in 60 ml of either acetonitrile or methyl ethyl ketone. The sample is titrated potentiometrically with 0.1 N perchloric acid in acetonitrile. Double potential breaks will be observed with N-methyl oxides.

Calculations:

$$\text{Amine oxide (meq/g)} = 2 \times \text{(meq/g of first break)}$$

$$= \frac{2\,[\text{Titer} \times \text{normality } (HClO_4)]}{\text{Sample wt. (g)}}$$

Free amine (meq/g) = (meq/g of second break)–(amine oxide meq/g)

RESULTS AND DISCUSSION

In this work a Sargent-Welch Model DG automatic titrator was used for the titrations. The traditional glass-calomel electrode system can be used, but it has a tendency to plug up in the nonaqueous solvent systems and consequently interferes with the titration. For this reason, we substituted a modified glass-platinum electrode combination. The best results were obtained when the reference electrode was placed in the titrant stream as shown in Figure 1. Bezinger replaced the standard calomel electrode with one containing lithium perchlorate in acetic anhydride (8).

Two commercial long chain dimethylalkylamine oxides, N-cocomorpholine oxide and ethoxylated amine oxides were used in this investigation. All of these commercial N-oxides contained some free amine. The composition of these products was verified by gas chromatography and thin layer chromatography. Only the amine oxides that had the N-methyl configuration gave two breaks in the titration. By spiking the sample with free amine it was determined that the free amine is titrated as part of the second half of the titration. This is the reverse of Bezinger's observations. Bezinger reported that the free amine is titrated as part of the first half of the titration (8). Some typical titration

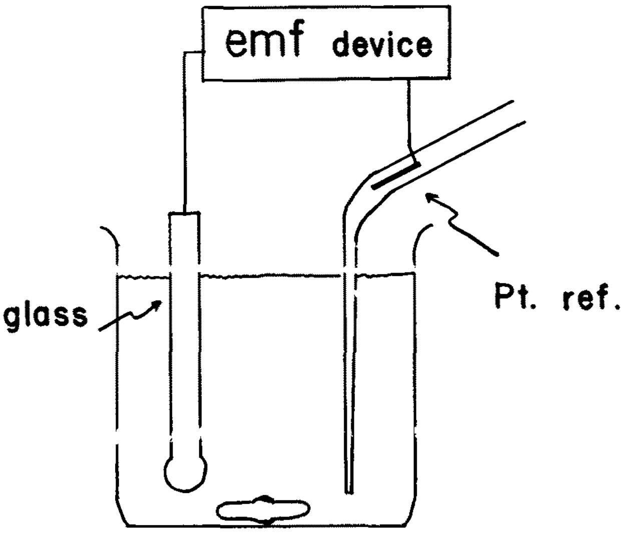

FIG. 1. Glass-platinum electrode titration system.

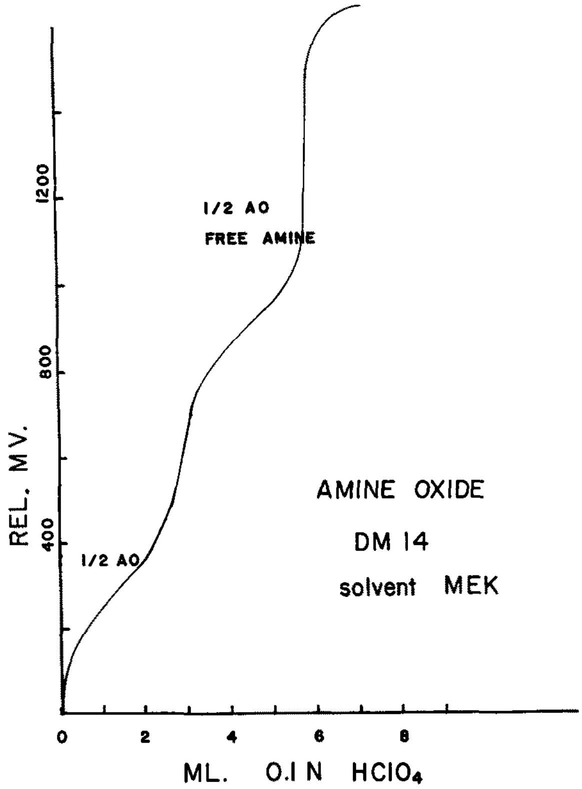

FIG. 2. Typical amine oxide titration curve.

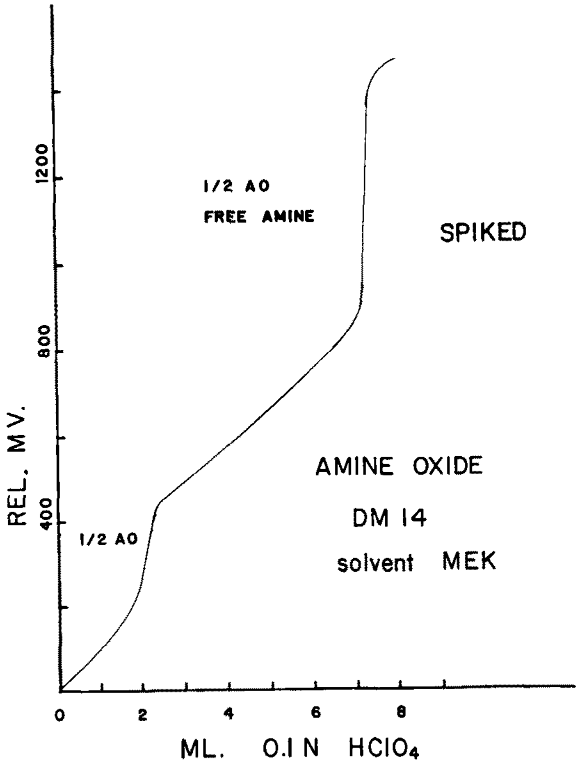

FIG. 3. Typical amine oxide titration curve with free amine added.

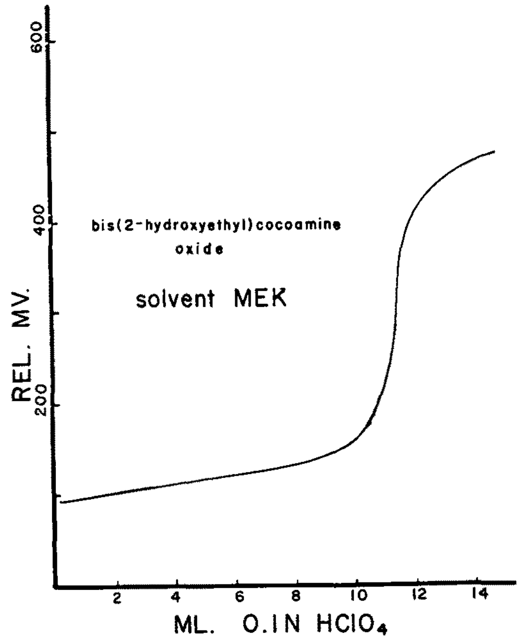

FIG. 4. Titration curve for amine oxide containing no N-methyl group.

curves for dimethylalkylamine oxides with and without added free amine are shown in Figures 2 and 3. A titration curve for ethoxylated amine oxide is shown in Figure 4. Only one potential break is observed in this titration of an amine oxide that has no N-methyl group.

Listed in Table I are some results obtained with several commercial dimethylalkylamine oxides. The results tabulated are the average of three determinations. The excellent precision obtained indicated the method showed promise as a rapid and simple quality control procedure for amine oxides containing the N-methyl group configuration, the most common commercial amine oxides.

In order to further study the recovery and precision of the method, a number of dimethylalkylamine oxide samples fortified with two levels of free amine were prepared. These samples were titrated using the described procedure. The results are shown in Table II. The results indicated that good recoveries of free amine in the presence of the related amine oxide can be obtained.

Any residual hydrogen peroxide appeared to have no effect on the titration. The method has the further advantage of giving the free amine and amine oxide with one titration. No derivatization steps are necessary as in some previously reported methods for determining free amine in amine oxides (5).

TABLE I

Titration Results of Commercial Dimethyl Alkyl Amine Oxides*

Sample	1st break (meq/g)	std. dev.	2nd break (meq/g)	std. dev.	Amine oxide (meq/g)	Free amine (meq/g)
Dimethyl tetradecyl amine oxide	0.568	0.001	1.182	0.001	1.136	0.046
Dimethyl hexyldecyl amine oxide	0.663	0.002	1.397	0.003	1.326	0.071
Dimethyl coco amine oxide	0.810	0.002	1.676	0.001	1.620	0.056

*Average of three determinations.

TABLE II

Recovery Study

Sample	Original amine present (meq/g)	meq/g amine added	meq/g amine found*	meq/g amine recovered	% Recovery
Amine oxide DM18	0.083 (2.5%)	–	0.083	–	–
Amine oxide DM18 spiked-1	0.083	0.163 (4.9%)	0.246	0.163	100 ± 0.5
Amine oxide DM18 spiked-2	0.083	0.106	0.188	0.106	100 ± 0.5

*Average of two determinations.

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