Titration of Long-Chain Quaternary Ammonium Compounds Using Tetraphenylboron[1]

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Abstract

A rapid macro procedure for the determination of long-chain quaternary ammonium compounds (QAC) has been developed using sodium tetraphenylboron as a titrant. About 1–1.5 meq of QAC is dissolved or dispersed in 50 ml of water. Dichlorofluorescein is added as an indicator. The sample is then titrated with 0.06 N aqueous sodium tetraphenylboron. As long as free QAC is present the mixture will be pink. When the tetraphenylboron has reacted with all of the QAC, the indicator becomes yellow. The procedure has been used routinely to analyze both pure and commercial QAC with good results. The possible interferences include amine salts and potassium ion. The amine salt interference may be easily corrected or eliminated by changing the pH. The method has also been applied to the determination of a variety of quaternary ammonium salts having anions other than halides.

Introduction

In the synthesis and manufacture of long chain quaternary ammonium compounds (QAC) it was desired to control these products by a macro-titration procedure. A technique that would be analogous to an acid value in fatty acid production control would be very useful. The most common procedures for titrating quaternary ammonium compounds use anionic detergents as the titrant (6). Two phase solvent systems, such as chloroform and water, are used with various indicators, usually bromophenol blue, methyl orange, methyl yellow, or methylene blue. A system of titrating QAC with perchloric acid in the presence of mercuric acetate has found considerable popularity (12). Another perchloric acid procedure using acetic anhydride solvent was recently reported (13).

A number of colorimetric procedures have been devised based on the reaction of the cationic salt with an anionic dye (1,3,7). This dye complex is usually extracted into a water immiscible solvent such as chloroform. The absorbance of the color may then be measured with a spectrophotometer. Other procedures include precipitation of the QAC followed by titration of the excess ferricyanide (9,15). The anionic detergent titration procedures and the anionic dye colorimetric methods are essentially micromethods. They are quite useful at the low QAC use levels. However, they are not easy to use as control procedures. The perchloric acid procedures not only titrate the quaternary ammonium salts (halides, acetates, and nitrates), but also titrate the inorganic salts often found in commercial QAC salts. Ashing the sample is usually required to correct for inorganic salts. Furthermore, these perchloric acid titration procedures fail when the anion is sulfate.

A number of analytical methods for the determination of potassium have been based on the reaction of QAC with sodium tetraphenylboron to give insoluble salts (5,14). These authors suggested that the procedure might be modified to be used for the analysis of the QAC itself. Several two-phase procedures for QAC using tetraphenylboron as a titrant have been reported (2,11). A precipitation procedure for QAC utilizing sodium tetraphenylboron was also reported (10). A volumetric procedure for QAC with sodium tetraphenylboron as a titrant and methyl orange as an indicator at a pH range of 3.1–4.0 has been described (16). Cross (4) made an extensive investigation of the qualitative and quantitative determination of cationic surface active agents using sodium tetraphenylboron.

It was decided to explore the possibility of using the tetraphenylboron reaction as the basis for a direct titration of QAC that would meet our needs. A simple and rapid procedure for QAC was devised using sodium tetraphenylboron as a precipitating titrant. The titration is done in a one-phase system (water). The pH range of the method is very broad and no buffered solvent system is required. The indicator used is 2′, 7′ dichlorofluorescein which gives an extremely sharp color change from pink to yellow at the endpoint. Since macro sample sizes are weighed and titrated, the method is readily applicable to plant control work. The method is as simple to used as an ordinary acid value determination. The procedure will also titrate amine salts. However, in QAC samples these can readily be corrected or eliminated by neutralization of the amine salt.

Experimental

Reagents

Sodium Tetraphenylboron Solution. Twenty-three grams of reagent grade sodium tetraphenylboron (Bakers Analyzed) is dissolved in 500 ml of distilled water. The mixture is stirred vigorously and allowed to stand for at least one hour. The solution is then filtered through a Gooch crucible. Sufficient water is added to make one liter. Two milliliters of 20% sodium hydroxide is added to this standard solution as a stabilizer. The solution is standardized against a high purity quaternary ammonium halide. The normality will be approximately 0.07 N. This solution often has a slight haze which does not hinder its effectiveness.

Indicator. 2,7 dichlorofluorescein, 0.2% in ethanol.

Powdered Sucrose. Baker Analyzed Reagent.

Procedure

A QAC sample of 2–3 mmoles is weighed into a 150 ml beaker and dissolved in 40 ml of water. If the sample is insoluble in water, it is first dissolved in a minimum of isopropyl alcohol. Then 40 ml of water is added to the solution to thoroughly disperse the quaternary ammonium compound in the solvent. Complete solution is not necessary. A minimum of alcohol is desirable in the system since it may sometimes interfere with the endpoint. About 0.5 g of

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powdered sucrose is added to the system to help prevent coagulation of the precipitate. About 0.5 ml of dichlorofluorescein indicator is added to the beaker. The sample is then titrated with the sodium tetraphenylboron solution to a yellow end point. The color change is very sharp and the indicator usually turns a deep pink color just before the end point is reached.

This reagent will react with amine salts if they are present in the sample. A correction for amine salt is made by running a separate titration and subtracting the equivalents found with the titration. A 5 g sample is weighed into a 150 ml beaker and dissolved in 40 ml of isopropyl alcohol. This sample is then titrated with 0.1 N sodium hydroxide to a phenolphthalein end point.

Calculation

A = milliequivalents/gram tetraphenylboron titration

B = milliequivalents/gram sodium hydroxide titration

$$\% \text{ Quaternary ammonium compound} = \frac{(A - B) \text{ mol wt QAC}}{10}$$

Molecular Weight Determination of QAC Using Tetraphenylboron Salt

The precipitate from the QAC titration is filtered, washed and dried. A sample of this dried precipitate is then weighed into a 150 ml beaker. The sample is dissolved in a small amount of dioxane and 50 ml of glacial acetic acid is added. If necessary heat on a steam bath to effect solution. The sample is then titrated with 0.1 N perchloric acid in glacial acetic acid. Either a crystal violet end point or a potentiometric endpoint may be used.

Calculation

$$\text{Neut. Equiv. of QAC-TPB salt} = \frac{\text{Sample wt gram} \times 1000}{\text{Normality } HClO_4 \times \text{ml titration}}$$

$$\text{Mol wt of QAC} = \text{N.E.} - 319.35 + \text{mol wt of anion}$$

Results and Discussion

A number of indicators have been recommended for titrating with QAC's. Schall (14) used bromophenol blue in his procedure for potassium which used a QAC to back titrate the excess tetraphenylboron. Epps and Burden (5) claimed Clayton Yellow was superior to bromophenol blue as an indicator. Both of these procedures used quaternary ammonium salts as titrants and were not designed for the titration of QAC with sodium tetraphenylboron. We had great difficulty seeing the end point with either of these indicators using the described procedure. Uno used methyl orange and several other indicators (16). Although the end points of several of these indicators were fairly easy to see, they are all dependent on buffered systems of a narrow pH range. Many indicators were tested by us in this titration. The one indicator that performed most satisfactorily was 2′, 7′ dichlorofluorescein. This dye forms a characteristic pink complex with QAC's. With the complete precipitation of the QAC with sodium tetraphenylboron, the pink color of the indicator complex suddenly changes to yellow. This change occurs throughout a large pH range for the samples. However, the final pH of the solution usually ends up on the basic side because of alkaline preservative in the sodium tetraphenylboron.

TABLE I

Comparison of the Tetraphenylboron Titration with the Perchloric Acid Titration of Quaternary Ammonium Compounds

	Found %	
	Na TPB[a]	Perchloric acid
Trimethyl octadecylammonium chloride	99.8 ± 0.1	99.9
Dimethyldidodecylammonium chloride	96.8 ± 0.1	97.3
Dimethyldihexadecylammonium chloride	99.4 ± 0.1	99.1
Dimethyldioctadecylammonium chloride	97.8 ± 0.1	98.9
Trimethyldodecylammonium chloride	100.0 ± 0.1	99.9
Arquad 0–50	51.8	52.3
Arquad 18–50	50.9	50.7
Arquad T–2C	73.0	75.7

[a] Average of three determinations.

TABLE II

Comparison of the Tetraphenylboron vs Sodium Lauryl Sulfate Titration of Quaternary Ammonium Compounds

QAC	TPB	Sodium lauryl sulfate
Arquad 12/50	49.6	49.8
Arquad 18/50	52.4	51.4
Arquad 0/50	50.0	51.1
Arquad T/50	51.5	51.7
Arquad 2C/75	76.3	77.4
Arquad 2HT/75	75.6	76.3

The titration works best in a completely aqueous solvent system. The precipitate is somewhat soluble in organic solvents. This solubility prevents the necessary equilibrium systems that are required for a quantitative analytical scheme. The quaternary salt must be completely removed from the system to cause the indicator change. Small amounts of alcohol (less than 10%) may be tolerated if an organic solvent is required for good dispersion of the sample in the water system. It is interesting to note that complete solubility of the sample is not necessary to obtain good results. However, QAC's such as dimethyldioctadecyl ammonium chloride should be dispersed as finely as possible for best results.

Any cations that form precipitates with sodium tetraphenylboron are possible interferences. In practice we found we had to be concerned only with amine salts. In the commercial manufacture of quaternary ammonium compounds sodium chloride is usually found as an impurity. Potassium ion is normally not found in these samples and thus is not an interference problem. However, if amine salts are neutralized with caustic to eliminate them as an interference, potassium hydroxide must not be used in this operation.

A number of purified and commercial quaternary ammonium compounds were analyzed by both the tetraphenylboron titration and the perchloric acid procedure. The results of the two procedures which compare favorably, are shown in Table I. A second series of commercial quaternary ammonium com-

TABLE III

Titration of Different Types of Commercial Quaternary Ammonium Compounds using TPB

	% Found	Theory[a]
Dimethylbenzyloctadecylammonium chloride	93.1	95.0
Dimethyldi-"Hydrogenated Tallow" methyl ammonium sulfate	75.7	75.0
Methyl bis-2-hydroxyethyloctadecylammonium chloride	99.8	100.0
Octadecylamidopropyldimethyl-2-hydroxyethyl ammonium nitrite	43.5	50.0
Methyl benzyl di-"Hydrogenated Tallow" polyethoxy (7) ammonium chloride	78.5	75.0
Hyamine 10X; p-(diisobutyl-cresoxyethoxyethyl) dimethyl benzyl ammonium chloride	100.1	100.0

[a] Activity claimed by manufacturer.

TABLE IV

Titration of Purified Amine Salts

	Original method	Modified method[a]
Dodecylammonium chloride	84.3	99.6
Tetradecylammonium chloride	85.4	99.3
Dodecylammonium acetate	84.5	96.9

[a] One ml of 0.2 N HCl was added to sample.

pounds were analyzed by the TPB method and also by partition titration using a sodium lauryl sulfate titrant. The results are shown in Table II and the agreement between the two methods is good.

The method is independent of the anion or alkylating group used to make the QAC. This is demonstrated in Table III which gives results for a number of different QAC's having benzyl groups and anions other than chloride. Of particular interest is the quaternary salt containing a polyoxyethylene group. QAC's containing polyoxyethylene groups often form dye complexes that are very water-soluble and cannot be extracted into the organic phase in partition analytical systems. Several quaternary ammonium salts of this type were tested with good results.

Since the amine salts interfere with the determination of QAC's, this suggested a possible method for determining amine salts in amines. A number of pure amine salts were prepared and titrated using the described procedure. The results are shown in Table IV. It was found that the pure amine salts were not titrated quantitatively with the unmodified procedure. The caustic stabilizer neutralized some of the amine salt and this in turn was unreactive to TPB. It was found that the procedure had to be modified by adding enough acid to neutralize the sodium hydroxide stabilizer in the tetraphenylboron solution that was required for the titration.

The quaternary tetraphenylboron precipitate may be used for determining the molecular weight of the original QAC. The precipitate is recovered and dried. Portions of this material may be dissolved in glacial acetic acid. This solution may then be titrated with standard perchloric acid in acetic acid potentiometrically or to a crystal violet end point. On subtracting the tetraphenylboron molecular weight from the neutralization equivalent the molecular weight of the quaternary ammonium cation is obtained. Table V gives the molecular weight results obtained with several purified and commercial QAC's. The agreement of the found results with the calculated values was very satisfactory. With this analytical system one can find the equivalents of QAC in an unknown sample. The precipitate may then be recovered to determine the molecular weight of the original QAC.

TABLE V

Molecular Weight Determination of Quaternary Ammonium Compounds Using their Tetraphenylboron Salts

	Mol wt	
	Found	Calculated
Trimethyloctadecylammonium chloride	346.1	347.5
Trimethyldodecylammonium chloride	264.2	263.5
Dimethylbenzyloctadecylammonium chloride	418.1	423.6
Dimethyldioctadecylammonium methyl sulfate	659.3	648.0

In our laboratory the sodium tetraphenylboron solution was standardized against a trimethyloctadecylammonium chloride of high purity. This particular compound was synthesized in our laboratory. However, Hyamine 10X or benzethonium chloride of high purity is available commercially and may be used as primary standards. The Hyamine 10X gave a sharp end point, but the precipitate formed adsorbed some of the dye and remained pink. Unless the operator is aware of this, the end point can be somewhat obscured.

REFERENCES

1. Auerbach, M. E., Ind. Eng. Chem. Anal. Ed. *15*, 492 (1943).
2. Boden, H., Chemist Analyst *52*, 112 (1964).
3. Colichman, E. L., Anal. Chem. *19*, 430 (1947).
4. Cross, J. T., Analyst *90*, 315 (1965).
5. Epps, E. M., and J. C. Burden, Ibid. *30*, 1882 (1958).
6. Epton, S. R., Nature *160*, 756 (1947).
7. Few, A. V., and R. H. Ottewill, Colloid Science *11*, 34 (1956).
8. Gautier, J. A., J. Renault and F. Pellerin, Ann Pharm. Franc. *13*, 725 (1955).
9. Hefferren, J. J., and C. Dietz, J. Pharm. Sci. *50*, 535 (1961).
10. Kirsten, W. J., A. Berggren and K. Nilsson, Anal. Chem. *30*, 237 (1958).
11. Patel, D. M., and R. A. Anderson, Drug Standards *26*, 189 (1958).
12. Pifer, C. W., and F W. Wollish, Anal. Chem. *24*, 300 (1952).
13. Puthoff, Mary Ellen and J. H. Benedict, Anal. Chem. *36*, 2206 (1964).
14. Schall, E. D., Anal. Chem. *29*, 1044 (1957).
15. "United States Pharmacopeia" *16th* rev., Mack Publishing Co., Easton, Pa., 1960, p. 82.
16. Uno, T., K. Miyajima and H. Tsukatani, Yakogako Zasshi *80*, 152 (1960).

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