Potentiometric Titration of Long Chain Quaternary Ammonium Compounds Using Sodium Tetraphenyl Borate[1]

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Current methods for determining the activity of long chain quaternary ammonium compounds (QACS) are based either on dye partition, titration, or colorimetric analysis. The two major disadvantages of these methods are the disparity of partition coefficients among differently constituted QACS and the difficulty in detecting visual end points. Some potentiometric titration methods for QACS have been reported in the literature. However, back titration techniques, as well as complicated electrode systems, are generally involved.

A new potentiometric titration system is presented which uses aqueous sodium tetraphenylborate (TPB) solution as a titrant and a platinum-platinum electrode system to detect the end point. Standard potentiometric titration instruments may be used for this method. This new potentiometric method is superior in precision and accuracy to visual (colorimetric) methods.

During the production of long chain quaternary ammonium compounds, fast yet accurate analytical methods are needed to control the process. They are also needed to determine the activity in order to meet trade specifications. There are several methods currently being used for these purposes. One is the titration of quaternary ammonium compounds by anionic surfactants using two-phase immiscible solvent systems and visual indicators (1,2). Alternately, a number of colorimetric procedures have been devised based on the reaction of the long chain cationic salt with an anionic dye (3-6). Direct titration of any halide-containing QACS using perchloric acid as a titrant and acetic anhydride as a solvent has been reported (7,8).

Thermometric titration as well as membrane electrode titration systems have recently been reported for determining QACS (9-16). However, the low solubility of QACS containing two long chains make it impossible to use membrane electrode systems to analyze these very important classes of QACS.

A number of analytical methods developed for QACS are based on titration with sodium tetraphenylborate or silver nitrate using either zero current potentiometry or amperometry for end point detection (17-22). Most of these methods are not direct titrations of the QACS cation. They are indirect methods in which the anion is measured or back titration techniques are used. Sodium tetraphenylborate (TPB) has found wide applications in the analytical chemistry of univalent cations because of the negligible solubility of many of the tetraphenylborate salts. Methods using the tetraphenylborate ion are used for the determination of potassium, rubidium and other metal ions (20,23-25). TPB has also been used to precipitate basic organic nitrogen compounds for qualitative identification of these materials (17,26,27).

Metcalfe *et al.* (28) reported the titration of long-chain quaternary ammonium compounds using sodium tetraphenylborate as a titrant and 2′, 7′ dichlorofluorescein as an indicator. This method has been used in our laboratory for many years to analyze common long-chain QACS. However, some QACS could not be analyzed with this method, mainly because of fading end points and uncertain visual indicator color changes.

The method described here utilizes the above tetraphenylborate titration, but improves the end point determination by the use of potentiometric detection with platinum-platinum electrodes. Excellent results have been obtained, indicating that this new procedure promises to be a superior technique for the determination of long-chain quaternary ammonium compounds.

MATERIALS

Sodium tetraphenylborate solution. Twenty-five grams of reagent grade sodium tetraphenylborate (Aldrich Chemical, Milwaukee, WI) was dissolved in 1000 ml of distilled water with stirring. The solution, which is approximately 0.07 N, is allowed to stand overnight before standardization. The solution sometimes has a slight haze which does not effect its use as a titrant. The TPB solution is standardized using crystalline Hyamine 1622 (Diisobutylphenylphenoxyethoxyethyldimethylbenzyl ammonium chloride monohydrate; Lonza, Fair Lawn, NJ) following the procedure described for samples.

Commercial long chain quaternary ammonium salts, Arquad 18 (Octadecyl trimethyl ammonium chloride) and Arquad 2HT (Dihydrogenated-tallow-dimethylammonium chloride), products of Akzo Chemical Division (Chicago, IL) were used. The glacial acetic acid is A.C.S. reagent grade.

For this study a Sargent-Welch Model DG automatic titrator was used, although any automatic titrator or pH meter can be used with the described electrode system. This electrode system consists of one platinum ring electrode, the indicating electrode which is placed in the titration vessel. The reference platinum electrode is inserted into the titrant stream. This was done by inserting a small platinum wire into a plastic tube that was used to connect the burette and the burette tip. It is important to keep the burette tip immersed in the titrated solution at all times. An alternate electrode system using commercially available electrodes may also be used. In both cases, the indicating electrode may be either a platinum ring prepared from platinum wire or a large surface platinum electrode (Metrohm type 6.0305.010). A double junction silver/silver chloride electrode containing a 0.2 Molar sodium chloride solution as the outer electrolyte (Orion) may be used as an alternative reference electrode.

METHODS

A sample containing about 1.5-2.0 milliequivalents of the long chain quaternary ammonium salt is weighed into a

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150 ml beaker, dissolved in 5–10 ml of glacial acetic acid and diluted with 60–80 ml of hot water. The sample is then titrated potentiometrically with standardized sodium tetraphenylborate solution using one of the described electrode systems. The quaternary content expressed in milliequivalents per gram is obtained from the milliliters of titrant multiplied by its normality and divided by the sample weight.

After the titration, the electrode and the burette tip are rinsed with acetone and then water to remove any of the TPB salts that may have deposited on the surfaces. This step is very important, as the sensitivity of the electrode will be reduced for subsequent titrations.

RESULTS AND DISCUSSION

This potentiometric TPB method was compared to the visual TPB titration method of Metcalfe *et al.* (28). Three chemists, using both methods, analyzed a sample of dihydrogenated-tallow-dimethylammonium chloride (Arquad 2HT) 25 times, and a sample of octadecyl trimethyl ammonium chloride (Arquad 18) 10 times. The data obtained are shown in Tables 1 and 2. The standard deviation analysis shows that the precision of the potentiometric method is better than that of the visual method.

TABLE 1

Comparison of the Potentiometric vs the Visual Titration of a Dihydrogenated Tallow Dimethyl Ammonium Chloride (75%) Using Tetraphenylborate Titrant

Method	N	Mean (meq/g)	Std. dev.
Potentiometric	25	1.422	0.007
Visual	35	1.417	0.032

TABLE 2

Comparison of the Potentiometric vs the Visual Titration of a Octadecyl Trimethyl Ammonium Chloride Using Tetraphenylborate Titrant

Method	N	Mean (meq/g)	Std. dev.
Potentiometric	10	2.817	0.009
Visual	10	2.807	0.030

TABLE 3

Comparison of the Sodium Lauryl Sulfate Titration vs the Potentiometric Tetraphenylborate Titration for Quaternary Ammonium Compound

Method	Sample	N	Mean (meq/g)	Std. dev.	Correlaton coefficient
TPB-POT	A	10	1.7429	0.0066	Approx. 1
SLS-VIS	A	10	1.7140	Aliquots only, no std. dev.	—

A: Dihydrogenated tallow dimethyl ammonium chloride, 100%. TPB: Sodium tetraphenylborate titrant. SLS: Sodium lauryl sulfate titrant. POT: Potentiometric method. VIS: Visual titration.

The improvement in precision is not unexpected. Although visual TPB titration can be very accurate and precise, the method is dependent on the type of QACS being analyzed. Fading and inconsistent end points often occur with difunctional and highly ethoxylated quaternaries. In contrast, the titration curves from this improved method are reproducible and consistently shaped for a wide variety of QACS. Typically, titration curves exhibit potential breaks of at least 100 mv. Additionally, this potentiometric titration can be used to analyze quaternary acetates and sulfates as well as chlorides.

The potentiometric TPB titration was also compared to a two phase titration using sodium lauryl sulfate (SLS). The SLS procedure, discussed in several references (1–5), is a micro technique for QACS. The comparative data are given in Table 3. The two-phase titration method using sodium lauryl sulfate as the titrant has been used for many years. The SLS procedure is prone to errors from sequential sample dilution and volumetric transfers of very low concentrations of sample. The laborious end point determination makes over-titration the most common source of error. None of these error-sources are applicable to the TPB potentiometric titration.

As might be expected, a plot of titration volume against sample concentration is linear. However, the line does not pass through the origin. There is a small positive intercept on the volume axis that averages about 0.1 ml. This observation is common in many volumetric analytical procedures. If a large enough sample is taken the determinate error will be small. This was the approach taken in the described procedure. With small or unknown samples the error can be significant. This problem was addressed by two of the authors (Donkerbroek and Wang), and is reported elsewhere (29).

The electrode mechanism of the tetraphenylborate potentiometric titration is shown in the following equation:

$$[R_4N]^+ X^- + Na^+(TPB)^- \rightarrow R_4N \cdot TPB_{(S)} + Na\ X$$

We suggest that at the end point of this titration the concentration of the QACS in solution is exhausted and the concentration of the tetraphenylborate rapidly increases in the solution. The platinum electrode acts as a concentration cell responding to a potential change of about 100 mv caused by the excess concentration of tetraphenylborate ion.

The platinum-platinum electrode system preferred for this analysis has one major advantage over conventional cell designs. Since the reference electrode is not in the titration vessel, it cannot be contaminated or polarized. Further, the internal electrode is at a disadvantage, since it often contains potassium chloride which can leak into the system and be titrated by TPB, leading to inaccurate results. Also, the calomel electrode shows poorer potential response when compared to the platinum electrode.

In comparing the results obtained from these three procedures we have concluded that the potentiometric titration of long-chain quaternary ammonium compounds using sodium tetraphenylborate is superior in both precision and accuracy to the other methods examined.

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