The Analysis of Cationic Surfactants

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ABSTRACT

Long-chain cationic surfactants have become a very important class of industrial chemicals. These useful oleochemicals are usually based on vegetable oils and animal fats. They have many applications which include fabric softeners, antistatic agents, organo clays, emulsifiers, germicides, flotation chemicals, corrosion inhibitors and foam depressents. The fatty quaternary ammonium compounds (quats) are by far the most important of this group of the commercial compounds. However, the fatty amine salts and amine oxides must also be classified as cationic surfactants. Although not as widely used as quats, they have special properties and uses which are often unique and useful. The various analytical methods used for these chemicals serves several objectives, including routine quality control, identification and characterization, determination in mixtures and formulations, determination at use level, and determination in the environment. In general, the objective of the analysis will determine what method will be used. Routine quality control procedures will most often use wet methods or some simple instrumental techniques. Identification and characterization of unknown cationic samples often require the most sophisticated of instrumental and chromatographic methods. Use level and environmental samples usually must be analyzed using the most sensitive methods. Often, colorimetric analysis is adequate. These samples often must undergo rigorous separation and clean-up techniques before the method of choice can be used. The methodology for the analysis of fatty amines, amine oxides and quaternary ammonium compounds is reviewed with the various analytical objectives in mind. However, the main emphasis is placed on the quats.

ANALYSIS OF FATTY AMINES AND THEIR SALTS

Wet Methods

The commercial fatty amines include long-chain, primary, secondary and tertiary amines, diamines, amidoamines and imidoazolines. The amine salts most often encountered are the hydrochlorides, the acetates and fatty acids salts such as the oleates.

Wet chemical tests are most often used to control the manufacture of these products. Since the free amines are basic they are readily titrated with standard acids either colorimetrically or potentiometrically. The AOCS and ASTM have developed methods and have done collaborative studies on a number of these tests (1,2).

Table I shows the approved AOCS and ASTM wet tests for fatty nitrogen compounds. The most fundamental single analytical method is the amine value which is analogous to the acid value. The amine value is defined as the number of mg of KOH equivalent to the basicity in 1-g sample. With one simple titration, one can obtain amine value, apparent molecular weight or neutralization equivalent (NE) and percentage of amine if the molecular weight (MW) is known. Table II shows how this data can be calculated from one titration.

Primary, secondary and tertiary amines can also be determined by a series of differential titrations. This is usually accomplished by forming derivatives with the primary and secondary amines that do not titrate under normal conditions. Primary amines can form very weak Schiff's bases with aldehydes, leaving the secondary and tertiary amines that can be readily titrated. Tertiary amines can be titrated after removal of the primary and secondary amines by acetylation or reaction with phenylisothiocyanate.

The acid part of amine salts can be titrated using standard base such as KOH. If the acid is a relatively weak acid, such as acetic acid, the amine portion can also be titrated with strong acids such as hydrochloric or perchloric acid.

TABLE I

Approved Wet Chemical Test Methods for Fatty Nitrogen Compounds

Method	Designation AOCS	Designation ASTM
Total amine value of fatty amines:		
Potentiometric method	Tf 1a	D 2073
Indicator method	Tf 1b	D 2074
Primary, secondary and tertiary amine values of fatty amines:		
Potentiometric method	Tf 2a-64	D 2073
Indicator method	Tf 2b-64	D 2074
Percentage, primary, secondary and tertiary amines in fatty amines	Tf 30-64	D 2083
Iodine value of fatty amines, modified Wijs method	Tg 2A	D 2075
Iodine value of fatty quaternary ammonium chlorides modified Wijs method	Tg 3a	D 2078
Average molecular weight of fatty quaternary chloride	Tv 1a	D 2080

TABLE II

Data Calculated from a Single Titration of an Amine

$$\text{Amine value} = \frac{\text{mL} \times \text{N} \times 56.1}{\text{wt. g}}$$

$$\text{meq/g} = \frac{\text{N} \times \text{mL}}{\text{wt. g}}$$

$$\text{NE or apparent MW} = \frac{\text{wt. g} \times 1000}{\text{N. mL}}$$

$$\% \text{ Amine} = \frac{\text{mL} \times \text{N} \times \text{MW}}{\text{wt. g} \times 10}$$

Trace Amine Methods

Small quantities of amine salts in water can be determined colorimetrically using dye partition systems. The amine salts will form colored complexes with anionic dyes such as bromophenol blue, that can be extracted into chloroform or other water-immiscible solvents. Such methods are valuable, not only for low concentration of amine salts, but they are also useful in differentiating amine salts from quats. Both amine salts and quats will give colored extracts at acidic pH. However, only quats will give positive colors at higher or basic pH levels. There are probably 100 or more literature references for similar systems that are used to analyze low amounts of amines. However, there is no overall comprehensive review of these methods. Such a review would be a valuable addition to the literature.

A buffered indicator system we have found very useful for the dye partition analysis of small amounts of fatty amines is shown in Table III. Other similar systems use methyl orange, methyl yellow, metal complexes and many other color forming systems (2-4).

A modification of a method for small amounts of secondary amine can be applied to determining primary amine (5). This system for primary amines uses salicylaldehyde. A sample containing 3-18 mg of fatty amine

TABLE III

pH 3.5 Buffered Indicator for Amines

700 mL of 0.1 M aqueous citric acid
300 mL of 0.2 M aqueous disodium phosphate
50 mL of 0.2% bromophenol blue in methanol
50 mL of 0.2% bromocresol green in methanol

hydrochloride is dissolved in isopropyl alcohol and reacted with salicylaldehyde and NaOH at 60 C for 10 min. The sample is made acidic and the color read at 405 nm. The advantage of this system is that solvent partitioning is not required. Small amounts of the fatty primary amines can be determined in water.

Instrumental Methods for Amine Salts

The two instrumental techniques that are most useful for fatty amine analysis are gas chromatography (GC) and nuclear magnetic resonance (NMR). The gas chromatographic analysis of underivatized amines can be accomplished with base treated columns that use Apiezon greases, Carbowax 20M as liquid phases (6-8). Derivatization of the amines using trifluoroacetic anhydride, acetic anhydride or silylation makes it possible to use neutral columns such as DEGS to obtain separations of saturates and unsaturates and geometrical and positional isomers (9,10).

Proton NMR has been used to analyze mixtures of primary, secondary and tertiary amines in trifluoroacetic acid (11). More recently, carbon-13 NMR has been used to analyze fatty amines and their derivatives (12). With ^{13}C NMR, mixtures of primary, secondary and tertiary amines can be identified and quantified. Table IV shows the ppm shifts observed in the amine salts ^{13}C NMR spectra.

High performance liquid chromatography (HPLC) has been used to separate and analyze amines in the Armak laboratory. Liquid chromatography has been used mostly to separate the amines after derivatization with 3,5-dinitrobenzoyl chloride. With this derivative a sensitive UV detector can be used. Ethoxylated fatty amines have been analyzed by HPLC (13). Although we are aware of HPLC work being done on long-chain amines, very little has been published in this field. Excellent chromatograms of long-chain amines can be obtained using a reverse-phase C_{18} bonded silica column, and water/methanol gradient solvent systems.

Long-chain amine oxides. Some of the most interesting fatty nitrogen compounds are the long-chain amine oxides. They are used in many types of detergent formulations and other surfactant applications. The amine oxides are slightly less basic than amines. They show many of the characteristics of quaternary ammonium compounds. For example, they are often water-soluble, whereas the precursor tertiary amine will be quite water-insoluble.

Wet analytical methods. Most of the wet methods for amine oxides make use of their basicity. They can be titrated with standard hydrochloric or perchloric acid (14). One of the main analytical problems is differentiation between the precursor amine and amine oxide. One technique (15) reacts the residual tertiary amine with methyl iodide to form the neutral quaternary ammonium salt. The remaining amine oxide can then be titrated with HCl. Another method developed in our laboratories uses the Polonovsky reaction in which acetic anhydride reacts with the amine oxide to form a nontitratable compound. The remaining tertiary amine can then be titrated with standard acid.

In certain nonaqueous ststems, amine oxides will give two potentiometric breaks when titrated with perchloric acid (16). Benzinger and his coworkers found in using a dioxane/acetonitrile solvent, the first break represented the precursor residual amine and one half of the amine oxide in the sample. The second break represents the other half of the amine oxide. With this information it is possible to calculate the amine oxide and amine content quantitatively. For some reason, this technique has not been used very widely in the analysis of commercial amine oxides.

In similar work in our laboratory we have used both acetonitrile and MEK as solvents and 0.1 N perchloric acid in acetonitrile as the titrant. We observed two breaks for fatty amine oxides that have at least one N-methyl group. N-Alkylmorpholine oxides and ethoxylated amine oxides did not give two breaks. Furthermore, it was found that the first break was equal to one half the amine oxide and the second break was equivalent to the second half of the amine oxide plus any free amine present. This is just the reverse of Benzinger's observations. A full treatment of this work is planned for publication at a later date.

Trace Analysis of Amine Oxides

Most fatty amine oxides can be determined colorimetrically at very low levels with the same anionic dye, solvent partition systems used for long-chain amines. Other micro-analytical systems for amine oxides use sulfur dioxide decomposition (17), reduction with titanium (III) (18). However, these techniques do not lend themselves readily to quality control.

Chromatographic Methods for Analyzing Amine Oxides

Gas chromatography has been used to determine the chain length distribution and molecular weights of the amine oxides (19,20). The amine oxide will decompose (cope elimination) to form olefins or to form the precursor amine depending on the gas chromatographic conditions. In general, basic columns will cause formation of olefins and the use of neutral or acidic columns result in breakdown to tertiary amines.

Thin layer chromatography has also been used to separate amine oxides and amines. The spots may be visualized with charring (21), Dragendroff reagent (22) or Pinacryptol yellow (23).

HPLC has been applied to the separation of amine oxides and the free amines in our laboratory. Good chromatograms of *bis*-2-hydroxyethylococoamine oxide, have been obtained using a Bondapak C_{18} reverse-phase column and also with the short Waters radial Pak A column. With the first column, the solvent is methanol/0.1 M triethylamine: acetic acid, 75:25:0.3. With the second column, the solvent is methanol/PIC B7/$NaCH_3SO_4$, 80:10:10. The free amines are obtained using a different solvent system and an external standard is used for quantitation.

Analysis of Long-Chain Quaternary Ammonium Compounds

The long-chain quaternary ammonium compounds (quats) are a very important class of commercial chemicals. Con-

TABLE IV

A Comparison of Amines and Amine Salts Chemical Shifts

Type of amine	Type of carbon	Amine chemical shift (ppm)	Salt chemical shift (ppm)
R. . .CH_2–NH_2	–CH_2–	42.4	40.2
(R. . .CH_2)$_2$–NH	–CH_2–	50.3	47.8
(R. . .CH_2)$_2$–N	–CH_2–	54.6	52.8
R. . .CH_2–N(CH_3)$_2$	–CH_2–	60.2	58.0
	CH_3–	45.6	42.9
(R. . .CH_2)$_2$ NCH_3	–CH_2–	58.2	55.9
	CH_3–	42.5	40.0

sequently, there is a very large analytical literature on these compounds. One of the most complete reviews on the analysis of quats is by Cross (24). This work deals with qualitative and quantitative analysis isolation and instrumental analytical methodology.

Wet Analytical Methods for Quats

Volumetric analysis. Long-chain quaternary ammonium compounds will react or complex with anionic dyes and colored inorganic anions to give a colored species that can be extracted from an aqueous system into an immicible solvent such as chloroform. The fatty quats will do this over a broad pH range. This fact makes it possible to easily distinguish fatty amines from the quats. Both amines and quats will give colors with many anionic dyes in the organic phase under acidic conditions (pH 3). Only the quats will give color in the organic phase under basic conditions (pH 8). This property of the dye partitioning effect between water and an immiscible solvent has been made the basis for several titrimetric procedures.

Quats in water will form precipitates with anionic surfactants such as sodium lauryl sulfate, sodium dioctylsulfosuccinate or sodium cetylsulfate (25,26). In a two-phase solvent system, the quat anionic dye complex will eventually be split by the surfactant. The dye will transfer back to the aqueous phase from the organic phase. Many acid base indicators have been used for this titration. Bromophenol blue, methylene blue, methyl yellow, bromocresol green, eosin and its halogenated derivatives. In our laboratory we have long used sodium lauryl sulfate as a titrant and dichlorofluorescein as an indicator for the quantitative two-phase titration of many fatty quaternaries. More recent publications (27,28) use a mixture of disulfine blue VN and dimidium bromide. The biggest problem of all these methods is the slow or poor end-point. This problem requires a great deal of judgement on the part of the analyst. Toward the end of the titration, the titrant is added very slowly with considerable shaking of the sample. This is followed by time to allow the layers to separate so that the end-point can be seen.

Direct single-phase titrations of quats have advantages over the partition titrations. Several direct titration procedures have found wide use in industry. Quats with a halide or weakly acidic anion can be titrated with perchloric acid after being dissolved in glacial acetic acid containing mercuric acetate (29). A similar procedure uses acetic anhydride solvent and does not require the mercuric acetate (30). These methods are rapid and precise but cannot be used with sulfate quats.

Recently, the AOCS has been testing a system for titrating quaternaries that uses sodium tetraphenylboron (TPB) as a titrant (31). The titration is performed in water in the presence of dichlorofluorescein indicator. This indicator normally is yellow in aqueous solution, but in the presence of a long-chain quaternary a pink complex is formed. As TPB is added to the system, the quaternary precipitates. When all the quat is precipitated, the indicator suddenly changes from pink to yellow. The method can be used not only to determine the chloride quat but also the quaternary ammonium sulfate salts.

Colorimetric analysis. Many colorimetric procedures make use of the anionic dye extraction by quats into organic solvents. The same dyes mentioned earlier are used in these spectrophotometric methods, and have found wide use determining quats in waste water and environmental samples (32-34). The disulfine blue method seems to be the one most widely used today. At Armak we have developed a pH 5.6 buffered indicator system which has found wide use not only in our laboratory but in many other laboratories. This indicator is made by mixing 420 mL of 0.1 M aqueous citric acid, 580 mL of 0.2 M disodium phosphate, 50 mL of 0.2% bromophenol blue in methanol, and 50 mL of 0.2% bromocresol green in methanol.

Briefly the procedure generally used is as follows. The sample containing the quat is added to a 250-mL separatory funnel containing 20 mL of distilled water. Twenty mL of buffered indicator is added, followed by 20 mL of chloroform and 50 mL of distilled water. The funnel is shaken and the presence of a yellow color in the chloroform layer indicates the presence of a quaternary. The color intensity is read at 425 nm. Modifications of these colorimetric procedures can be made by varying the amount of solvent. Smaller amounts of solvent increase the sensitivity of the method; larger amounts decrease it. Standard calibration curves are developed using pure quats similar to that being analyzed. These colorimetric procedures have found wide use in determining trace amounts of many types of quats. These include monoquats of one, two and three long chains. Diquats, amidoquats and imidazoline-type quaternaries have been analyzed in this way. Ethoxylated and propoxylated quats can be analyzed with these methods up to ca. 8-10 moles of EO and PO. Above this the dye quat complexes become too water-soluble to be extracted or partitioned into the organic solvent.

INSTRUMENTAL METHODS FOR THE ANALYSIS OF QUATS

Gas Chromatography

Gas chromatography has been extremely useful in identifying the chain length distributions of long-chain quats. The quats are nonvolatile salts and must be converted to the tertiary amines which usually can be gas chromatographed quite easily. Warrington first debenzylated benzyl quats to obtain the tertiary amine (35). At Armak we found that the direct injection of a solution of the quats into the hot injection port of the gas chromatograph resulted in the breaking of the quat to tertiary amine (36). The tertiary amines emerging will give the chain length distribution and help with identification of the amine and consequently the quat. With one long chain quats the breakdown is almost quantitative. However, quats with two or more long chains break down in a more complex way. Because of this the pyrolytic GC method is only useful for qualitative identification.

Attempts have been made to do Hofmann degradations prior to GC analysis (37). These usually result in formation of olefins which must be related to the chain length distribution of the quaternary. This type of information is not too useful when the quats have more than one long chain. A simple method in which the methyl or benzyl halide could be removed to give the tertiary amine would be very useful for the gas chromatographic identification of quats. A variation of the method of Abidi (38) may prove useful. This method uses lithium triethylborohydride to remove the benzyl chloride. Perhaps it could be modified to do other types of quats as well.

High Performance Liquid Chromatography (HPLC)

HPLC is the most promising new analytical tool for quats. No derivatization or pyrolysis is required and the analytical conditions are very mild. The number of HPLC publications on the subject is relatively small. However, there is apparently considerable research going on throughout the world on HPLC of quats. One great advantage of HPLC is that the quats can be separated as classes (39). For example, one long chain and two long chain quats can be separated; benzyl quats from methyl chloride quats. This can be done on silica or cyanosilica columns. Using ion-exchange and

reverse-phase columns, the quats can be separated on the basis of chain length (40-42).

In the Armak Research Laboratory, HPLC is routinely used for the analysis of quats, such as dimethyldihydrogenated tallow ammonium chloride (Arquad 2HT). The column is μBondapak C_{18} and the solvent is methanol/water/acetic acid 95:5:0.3. This separation based on total carbons gives two sets of peaks, one long chain quat as impurities and the two long-chain quats (product). The separation of a quat mixture having one, two and three long chains is also possible. However, to obtain good analytical results, several separate chromatograms on alumina columns are required as of now. The solution to this HPLC problem that would require only a single chromatogram will be very useful in the industry.

Nuclear Magnetic Resonance (NMR) Analysis

In the Armak Research Laboratory we have found that carbon-13 NMR provides specific structural information on the quats. This information has been used for quantitative analysis of mixtures. The chemical shifts and T_1 value of the alpha carbon in quats having one, two and three long chains have been reported (43,44). A complex mixture with one, two and three long chains, can be analyzed using NMR. Carbon-13 NMR provides a simple method of analysis for this type of quat mixture which is difficult to analyze by either GC or HPLC. With a single spectrum it is possible to obtain both qualitative and quantitative data quickly and accurately. Table V shows the quantitative results of a known mixture of tallowtrimethyl (A) ditallowdimethyl (B) and tritallowmethyl (C) ammonium chlorides. One column shows the results with Nuclear Oberhauser Effect (NOE) and one without NOE. In general, without NOE, more accurate results can be obtained. However, it takes longer (2-3 hr) to obtain the same signal-to-noise ratio. With NOE, the results are reasonably accurate for most industrial analyses at a great saving in time.

TABLE V

Quantitative Determination of Mono-, Di-, and Trihydrogenated Tallow Quaternary Amines With and Without NOE

Type of quaternary	Standard weight %	With NOE weight %	Without NOE weight %
Mono-	29.3	29.0	29.4
Di-	31.2	30.8	31.1
Tri-	39.5	40.1	39.6

Ion Selective Electrodes for the Analysis of Quats

Many workers have long wished to have electrodes that are specific for cationic surfactants. The most successful work in this area has used liquid membrane electrodes that are sensitive to the large onium ions (45-47). These electrodes are usually used as sensors in titration systems utilizing sodium tetraphenylboron as a titrant. A number of other workers have developed ion selective electrodes for quats (48-50). However, these electrodes respond only to a limited number of quats and were not general in scope. Ion selective electrodes still belong to an area that requires more research.

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