# Potentiometric Titration of Sulfate in Some Typical Anionic Sulfonate and Sulfate Surfactants

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## Abstract

The inorganic sulfate content of several typical anionic surface active agents has been determined by a potentiometric titration with lead nitrate using the potassium ferri-ferro cyanide couple to detect the end point. The recovery of added sodium sulfate varied from $-6$ to $+5\%$ of the contained amount at the 0.5% sulfate level.

## Introduction

THE GENERAL METHODS for the determination of sulfate ion are dependent upon its removal from solution as a slightly soluble precipitate. Cations that have been used for this purpose include barium, lead, and benzidine. The resulting precipitate can be retained by filtration, washed, dried, and weighed. Even though these procedures are lengthy, the barium sulfate technique under properly controlled conditions is accepted as the standard method for the determination of sulfate. Additional procedures suitable for the determination of sulfate include the determination of excess precipitating cation, conductometric titrations, amperometric titration with lead nitrate, determination using an anion specific membrane electrode (1), a precipitation with excess lead and titration of the excess with $K_4Fe(CN)_6$ (potassium ferricyanide) and $K_3Fe(CN)_6$ (potassium ferrocyanide) using 4-amino-4′-methoxydiphenylamine hydrochloride as the redox indicator (2), colorimetrically by displacement of chromate from barium chromate (3), and a direct potentiometric titration with lead nitrate (4). Of the procedures listed, only (2) and (3) have been applied directly to surfactant solutions.

Direct determinations of sulfate in anionic sulfate-sulfonate surfactant solutions have been hampered mainly by the unpredictable nature of barium precipitates in this environment, interpretation of color changes in initially colored solutions, and the determination of the end point of a titration in solutions containing suspended solids. These encumbrances have been circumvented in the procedure reported in this paper in which sulfate is determined directly by a titration with lead and the end point of the titration is determined potentiometrically. The potentiometric indicator couple, ferri-ferro cyanide, was adopted from a method derived for soluble inorganic sulfate reported by Vogel (2).

In order to apply the Vogel procedure to surfactant solutions, three modifications were necessary. One, since detergent solutions frequently contain chloride in varying concentrations, the readily contaminated, chloride-sensitive Ag/AgCl reference electrode used by Vogel was replaced by a saturated calomel electrode (S.C.E.).

Two, the pH of anionic sulfate-sulfonates surfactant solutions is frequently basic, consequently proper acidification of the solution was necessary to prevent the precipitation of lead hydroxide during the titration. Three, lead sulfate is not sufficiently insoluble in water to yield good quantitative end points during a direct titration of sulfate with lead. The solubility of lead sulfate can be reduced by the addition of ethanol (Vogel); however, it was necessary to determine a water-to-ethanol ratio that would permit solubility of the sample and also be sufficiently rich in ethanol to reduce the solubility of lead sulfate. This procedure permits a rapid direct titration of sulfate in a broad spectrum of anionic sulfate-sulfonate surfactant solutions circumventing the difficulties encountered using indicators in solutions that are frequently colored and which contain a copious precipitate as a reaction product of the titration.

## Experimental

A known weight of sample was dissolved in a 1:1 solution of water and ethanol, acidified with dilute HCl, ferri-ferro cyanide indicator added, and titrated with lead nitrate. The end point was determined from the automatically recorded potentiometric titration curve or from a plot of the experimentally determined cell potentials.

### Apparatus

The titration was carried out in a 125-ml electroytic beaker fitted with a bright, platinum-wire indicating electrode and a saturated calomel reference electrode with a potassium nitrate salt bridge, and the solution was stirred with a magnetic stirrer. An E336 Potentiograph (Metrohm Ltd.; Herisau, Switzerland) was used to automatically record the titration curve. A Keithley Instruments 660A differential voltmeter was used to obtain the cell potentials existing during the titration. (Keithley Instruments, Inc.; Cleveland, Ohio). A Beckman platinum electrode (39186) and Beckman calomel electrode (40463) can be substituted for laboratory prepared electrodes.

Reagents were as follows: 1) Denatured ethyl alcohol. 2) 0.1 N HCl. Dilute 8.55 ml of 36% HCl to 1000 ml. 3) 0.02 M $Na_2SO_4$. Dissolve 2.84 g to the nearest 0.1 mg of anhydrous crystalline $Na_2SO_4$ in 1000 ml of distilled water. 4) 0.05 M $Pb(NO_3)_2$. Dissolve 16.562 g of anhydrous $Pb(NO_3)_2$ in 1000 ml distilled water. 5) 0.005 M $K_4Fe(CN)_6$. Dissolve 0.21 g of $K_4Fe(CN)_6$ in 1000 ml of distilled water. 6) 0.1 M $K_3Fe(CN)_6$. Dissolve 32.93 g of $K_3Fe(CN)_6$ in 1000 ml of distilled water. 7) 18-gauge platinum wire. 8) Mercury. 9) $KNO_3$, reagent grade. 10) Agar-agar.

## Procedure

All titrations were carried out in a solvent whose composition was 50 ml $H_2O$, 50 ml ethyl alcohol, 0.1 mg 0.005 M $K_4Fe(CN)_6$, 1 ml 0.1 M $K_3Fe(CN)_6$, and 3 ml of 0.1 M HCl. The solution was contained in a 125-ml electrolytic beaker and was stirred magnetically using a Teflon coated stirring bar. The titrant was standardized against a 25-ml aliquot of the

TABLE I
Potentiometric Titration of Sulfate in Some Anionic Surfactants

| Anionic surfactant | Mg $Na_2SO_4$ added | Mg $Na_2SO_4$ recovered | Per cent deviation | Mg $Na_2SO_4$ as $PbSO_4$ | Mg $Na_2SO_4$ as $BaSO_4$ |
|---|---|---|---|---|---|
| Linear alkyl benzene sulfonate | 28.4 | 26.5 | −6.7 | | |
| Linear alkyl ethoxy sulfate | 28.4 | 28.0 | −1.4 | | |
| Linear alkyl sulfonate | 28.4 | 29.8 | +5.2 | | |
| Secondary alkyl ethoxy sulfate | 28.4 | 28.2 | −0.7 | 28.3 | 29.6 |

standard sodium sulfate solution, correspondingly the water in the solvent was reduced to 25 ml. The potentiometric titration proceeded in a normal manner using either the laboratory prepared bright platinum wire electrode-saturated calomel electrode pair or the commercial electrodes (Beckman 38186 and 40463).

The platinum wire electrode was cleaned after each titration with fine emery paper, distilled water, and a soft towel. After each titration, the calomel electrode was washed with distilled water and wiped with a soft towel. Between titrations, the platinum electrode was stored in distilled water and the calomel electrode was stored in either saturated KCl or $KNO_3$ depending on the electrode that was being used.

A known weight of sample was taken to give an analytically suitable titration volume. The experimental conditions existing for this study required a 10-ml titrant volume for best results. After adding the sample to the previously described solvent-indicator solution, the sample was titrated in a manner analogous to the standardization procedure. The endpoint of the titration is determined by a graphical extrapolation of the two branches of the titration curve, i.e., the branch preceding and the branch following the inflection point.

## Calculations

$$\text{Molarity } Pb(NO_3)_2 = \frac{\text{Vol. } Na_2SO_4 \times Na_2SO_4 \text{ per liter}}{142.05 \times \text{vol } Pb(NO_3)_2}$$

$$\text{Per cent } H_2SO_4 = \frac{\text{Vol. } Pb(NO_3)_2 \times \text{molarity } Pb(NO_3)_2 \times 9.8}{\text{Sample weight}}$$

## Discussion

Neutralization of either an organo-sulfuric acid or an organo-sulfonic acid produces, in addition to the organic salt, the salt of any unreacted sulfuric acid. The process analyst and detergent formulator require a measurement of the inorganic sulfate content of the neutralized surface active agent. Sulfate can be determined as a constituent of the alcohol insolubles (5) or by a precipitation with lead nitrate followed by a back titration of the excess lead with $K_4Fe(CN)_6$ (2). The multistep procedures are satisfactory, but a direct determination is preferable. The potentiometric titration of sulfate with lead is based upon the insolubility of lead sulfate. The cell potential remains nearly constant as long as the ratio of ferri-ferro cyanide doesn't change. When the sulfate has been consumed, the next increment of lead precipitates $Pb_2Fe(CN)_6$, thus changing the cell potential and indicating the end point of the titration.

The direct potentiometric titration with lead nitrate has been applied to the determination of inorganic sulfate in the following surfactants: linear alkyl benzene sulfonate, linear alkyl sulfonate, linear primary alcohol ethoxy sulfate, and linear secondary alcohol ethoxy sulfate. Fig. 1 shows the titration curves obtained for these surface-active agents and a standardization titration of $Na_2SO_4$. Sodium sulfate was added to each of the four surfactants and the recovery is summarized in Table I.

The application of this procedure to surfactants

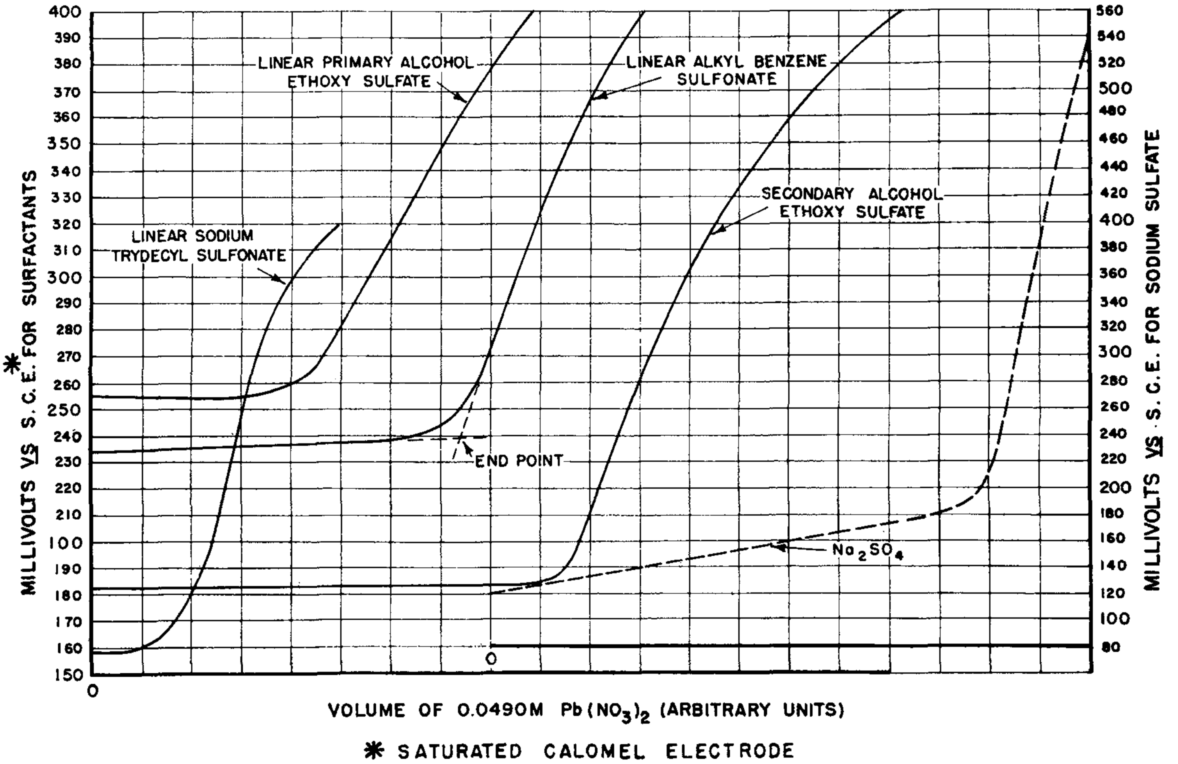

FIG. 1. Potentiometric titration of sulfate in some anionic surfactants.

TABLE II

Determination of Sulfate in Secondary Alkyl Ethoxy Sulfate—Precision of the Method

| | Percent sulfate |
|---|---|
| | 0.330 |
| | 0.340 |
| | 0.341 |
| | 0.344 |
| | 0.345 |
| | 0.346 |
| | 0.365 |
| Total | 2.411 |
| Mean | 0.344 |
| Standard deviation | ±0.015 |

was studied extensively for application to secondary alcohol ethoxy sulfates. Table I shows that the agreement between the direct potentiometric titration and gravimetric barium and lead results is acceptable. The precipitate from the potentiometric titration was isolated and identified using x-ray diffraction as $PbSO_4$. The precision of the method was determined using a sample of secondary alkyl ethoxy sulfate. A standard deviation of 0.015 was found for seven determinations listed in Table II. Needless to say, the speed of analysis was greatly increased using the direct titration. When the data were recorded automatically, weighing of the sample was the most time-consuming step.

### Limitations

Since this titration produces a precipitate, it is beset with all the absorption, coprecipitation, and occlusion processes characteristic of precipitation reactions. The interferences are minimized by keeping the volume of the precipitate to a minimun, maintaining a proper pH, the slow addition of titrant, making the proper choice of solvents, and adequate mixing of the solution. If the sulfate is removed from solution other than by precipitation with lead, the results will be low. On the other hand, consumption of lead by any other process yields high results, e.g., phosphate interferes in a positive manner. Using the same solvent mixture for the four different types of surfactants gave good recovery of added sulfate in all cases. Naturally, a prerequisite is that the anionic surfactant should not react with lead.

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