5 Analysis of anionics

5.1 Introduction

This chapter deals with the analysis of some individual anionic surfactants as raw materials and in some formulated products, or obtained as fractions separated by ion exchange or otherwise. It is assumed that materials obtained from unknowns will have been identified by spectroscopy or other means.

Anionic raw materials do not usually contain more than one surfactant species, and the determination of total active matter is usually straightforward, provided that the molecular weight is known. Anionics in formulated products can be determined without separation provided that no other ingredient interferes. Determination of mixtures with other surfactants, including mixtures of anionics, is covered in chapter 8.

Fractions obtained by anion exchange almost always contain other salts, as illustrated by the following examples.

1. Fractions obtained by removing cationics and amphoterics on a strongly acidic cation-exchange resin and neutralising the effluent contain salts of the anions of the cationics, and possibly anions of non-surfactant salts that were not removed by the initial extraction from the sample.

2. Fractions obtained by eluting from anion-exchange columns contain all the exchangeable anions from the resin. Hydroxide ions from a strongly basic resin eluted with hydrochloric acid emerge as water, and the excess acid is volatile, but if such an acidic eluate has been neutralised before evaporation it contains sodium or other metal chloride. Chloride ions from a weakly basic hydrochloride resin eluted with ammonia appear as ammonium chloride, which may be the chief constituent of the dried residue.

3. If the active has been converted to the free acid by passage through a strongly acidic cation exchanger, retained on a weak free base resin and then eluted with ammonia, the eluate contains the ammonium salts of any non-surfactant anions that were present in the sample.

The active matter can usually be isolated from such mixtures by drying and extracting with dry ethanol or propanol, but whether or not this is done, it will usually be necessary to determine the active by direct analysis. Section 5.2 gives some general methods, and the remainder of the chapter deals with methods for specific surfactant types.
All volumetric calculations required in this and subsequent chapters are performed by using the general equation given in section 1.4.1, and only those requiring some manipulation are written out in full.

5.2 General methods

5.2.1 Two-phase titration with benzethonium chloride

This is the most widely used method for total anion-active content, and was fully described in section 3.5. It can be used for raw materials, most formulated products, and without extraction for fractions from ion-exchange separations.

1. Weigh a sample containing about 1.5 g of anionic active. Dissolve in water, dilute to 1 l and mix.
2. Pipette 20 or 25 ml into a 100 ml stoppered measuring cylinder, a stoppered flask or the mechanical apparatus described in ISO 2271.
3. Add 10 ml water, 15 ml chloroform and 10 ml acid mixed indicator (disulphine blue VN and dimidium bromide).
4. Titrate with 0.004 M benzethonium chloride with thorough shaking or stirring after each addition until the pink colour is just discharged from the chloroform layer. If the chloroform layer becomes blue the end-point has been overshot.

If it is necessary to do the titration in alkaline solution, it may be easier to use the bromophenol blue method.

1. At step 3, replace the acid mixed indicator with 1.0 ml 0.04% bromophenol blue and 10 ml 0.1 M sodium hydroxide.
2. Titrate with 0.004 M benzethonium chloride with thorough shaking or stirring after each addition until the water layer is clear and colourless.
3. Carry out a blank titration on 25 ml water.

The blank titration should be 0.3–0.4 ml.

5.2.2 Potentiometric titration with benzethonium chloride

Construction of electrodes and experimental procedure were fully described in section 3.6. It is not recommended for fatty ester \( \alpha \)-sulphonates or carboxylates. Whilst \( \alpha \)-olefin sulphonates give good curves, it is uncertain which species is titrated. The method is satisfactory for many formulated products, but should be evaluated for individual applications. It is the method of choice when it is applicable. It is most conveniently done by autotitrator.