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Determination of Anionic Surfactants by Two-Phase Titration with Tetrabromophenolphthalein Ethyl Ester as Indicator

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ABSTRACT

A method has been developed for the determination of anionic surfactants in aqueous solution. It is based on solvent extraction titration of an ion pair. Zephiramine (tetradecyldimethyl ammonium chloride) is used as a titrant with tetrabromophenolphthalein ethyl ester as an indicator in the presence of chloroform. In the two-phase titration (chloroform/water), the proposed procedure gives sharp end-points as the organic phase changes from yellow to blue. The aqueous phase is colorless throughout the titration.

INTRODUCTION

The widespread use of synthetic anionic detergents has stimulated the development of numerous techniques for their determination in a variety of different systems. The most important among these methods are two-phase dye transfer methods using a cationic titration agent. A two-phase dye transfer titration method for the determination of anionic surfactants was initially proposed by Weatherburn in 1950 (1) using methylene blue as an indicator. Subsequently, a number of additional papers have been published, describing two-phase dye transfer procedures involving both modifications of the methylene blue method and methods substituting various dyes for methylene blue (2-6). Wang and Panzardi (2) published a general survey and background of two-phase titration and described a modified two-phase titration using azure A and methyl orange as the primary and secondary dyes, respectively. The dye transfer titration methods provide a means for rapid and accurate determination of anionic detergent active matter without the need for complex instrumentation. Titration end-point detection, however, can be a problem with the two-phase titration methods due to color reflectance between phases and differences in shade or hue of the color in the two phases. These problems occur because the end-point detection in the two-phase titrations is based on the transfer of the indicator dye from one phase to the other with end-points usually taken when color intensity is judged to be equal between the two phases.

The authors (7) recently developed a new extraction titration method based on the change of indicator in only one phase without movement of the indicator from one phase to the other, providing a sharp end-point and reducing the likelihood of error in accurately viewing the end-point.

EXPERIMENTAL PROCEDURE

Materials

The potassium salt of tetrabromophenolphthalein ethyl ester was dissolved in ethanol to make a 0.1% solution. Zephiramine (tetradecyldimethylbenzyl ammonium chloride) is available from Dojindo Laboratories, Kengun-Murazoe, Kumamoto, Japan and should be dried under reduced pressure before use (8). A stock solution of 0.01M zephiramine was prepared by dissolving 3.68 g of zephiramine (mol. wt. 368.0) in 1ℓ of distilled water. This stock solution was used to prepare standard solutions with the desired concentrations. Phosphate buffer solution, pH 6, was prepared from a 0.3 M disodium hydrogen phosphate solution by the addition of several drops of 10 N sulfuric acid using pH meter. Sodium laurylbenzene sulfonate, sodium lauryl sulfate, and Aerosol OT (di-2-ethylhexyl sodium sulfosuccinate) were obtained from Wako Pure Chemical Industries, Ltd., Dosho-Machi, Higashi-ku, Osaka, Japan and standardized by the two-phase dye transfer method described by Wang et al. (2).

Procedure

1-10 ml of 0.005 M sodium lauryl sulfate solution, 5 ml of phosphate buffer solution, 2-3 drops of tetrabromophenolphthalein ethyl ester solution (0.1%), and 10 ml of chloroform were placed in a 200 ml Erlenmeyer flask. Distilled water was added to make total volume ca. 25 ml. The mixture was titrated with 0.005 M zephiramine solution with intermittent shaking by hand to ensure equilibrium between the organic solvent and aqueous phase.

The initial mixture of sodium lauryl sulfate, buffer solution, tetrabromophenolphthalein ethyl ester indicator, and chloroform yields a solution with a colorless aqueous layer and a yellow chloroform phase. As the solution is titrated with zephiramine with thorough shaking after each addition of titrant, the chloroform solution turns green near the end-point. When one drop of excess zephiramine is added, the chloroform phase changes to a sky blue color indicating the end-point of the titration. The upper aqueous layer remains colorless throughout the titration, due to the water insolubility of the tetrabromophenolphthalein ethyl ester indicator.

RESULTS AND DISCUSSION

In the two-phase titration method described in this paper, a cationic titrant (tetradecyldimethylbenzyl ammonium chloride, NR_4+) is used with tetrabromophenolphthalein ethyl ester as the indicator (Ind). When anionic surfactants (AS) such as sodium laurylbenzene sulfonate, sodium laurylsulfate, or Aerozol OT (di-2-ethylhexyl sodium sulfosuccinate) are titrated with quaternary ammonium ion (NR_4+) solution, the $[NR_4{+}\cdot AS^-]$ complex is formed in the organic layer. The end-point of the titration is described by the following equation:

$$[NR_4+]\,aq + \underset{\text{yellow}}{[Ind]\,org} \rightarrow \underset{\text{blue}}{[NR_4{+}\cdot Ind^-]org} + H^+$$

A proteon of hydroxyl in nondissociated Ind (yellow) is substituted by NR_4+ to form an ion-pair $NR_4{+}\cdot Ind^-$ in

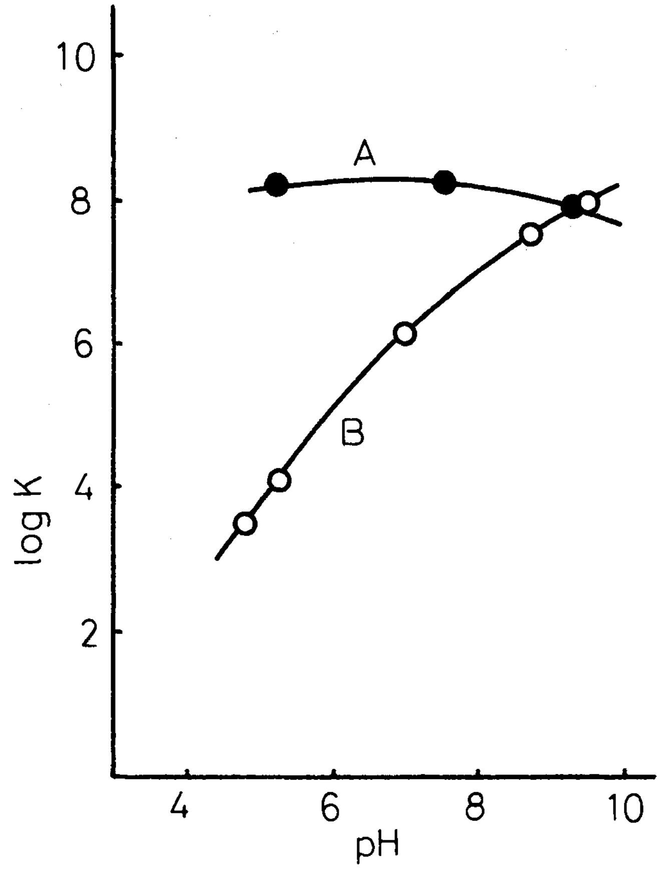

FIG. 1. LogK - pH diagram. A: $\log K_{LZ}$ B: $\log K_{ZIn}$.

which the indicator may be in dissociated form (blue).

The basic equilibria for the titration can be represented by:

$$L_w + Z_w \rightleftharpoons (LZ)_0$$

$$Z_w + In_0 \rightleftharpoons (ZIn)_0$$

where L is the lauryl sulfate ion, Z is zephiramine ion, In is the indicator, o is the organic phase, and w is the aqueous phase. The corresponding equilibrium constants are:

$$K_{LZ} = [LZ]_0 / ([L]_w \times [Z]_w)$$

$$K_{ZIn} = [ZIn]_0/([Z]_w \times [In]_0)$$

The effect of pH was studied by titrating a series of sodium lauryl sulfate solutions at various pH values. The titer was constant when the pH of the aqueous phase lay within the range 5.0-7.0. The effective stability constants can be obtained by determining $[LZ]_0$ and $[ZIn]_0$ using spectroscopic absorption measurements at various pH values (9). A simple logK-pH diagram is given in Figure 1 for the titration. Line A represents pL,-log$[L]_w$, at two equivalents of zephiramine where $[Z]_w = [LZ]_0$. Line B corresponds to the pZ,-log$[Z]_w$, value at which $[ZIn]_0 = [In]_0$. From the logK-pH diagram, a theoretical titration curve is constructed for the 0.01 M zephiramine titration of 10 ml of 0.01 M lauryl sulfate at pH 6 value as shown in Figure 2. The shaded areas indicate the region of the color change of tetrabromophenolphthalein ethyl ester indicator, B corresponding to the point of 50% color change. A maximum color change is obtained by a minimum increment of titrant at this point. The fractional color change from 0.1 to 0.9 covers about 2 pL units. The titration curve at pH 6 is not too far from the ideal case. Larger amounts of buffer solution had no influence on the titration, but amounts of less than 1 ml caused problems in phase separation. The effect of water-immiscible solvents on the titration were tested: nitrobenzene, methyl isobutyl ketone, butyl acetate, isoamyl alcohol, 1-2-dichloroethane, chloroform, toluene, benzene, carbon tetrachloride, chlorobenzene, and n-hexane. Of these, chloroform was the best solvent for the

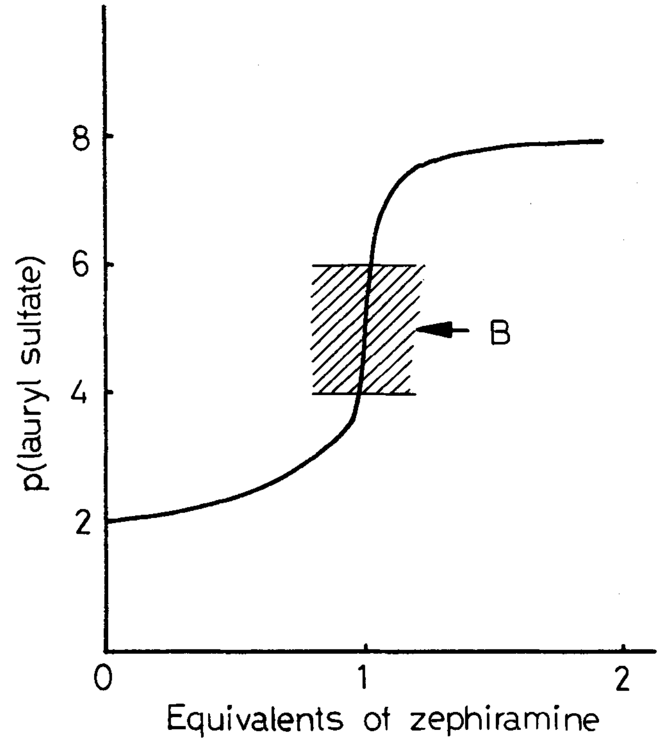

FIG. 2. Titration curve at pH 6.

TABLE I

Effect of Concentration of Zephiramine as a Titrant

Zephiramine (M)	Lauryl sulfate Added (mg/10ml)	Lauryl sulfate Founded (mg/10ml)
0.01	30.28	30.43
0.005	15.14	15.14
0.002	6.06	6.06
0.001	3.03	3.03
0.005	1.51	1.48

TABLE II

Evaluation of Two-Phase Titration by the Proposed Method and Dye Transfer Method[a]

0.0052M Lauryl benzene sulfonate		0.0051M Aerosol OT	
Proposed method	Azure A method(2)	Proposed method	Methylene blue method(1)
10.40	10.40	10.20	10.40
10.40	10.40	10.20	10.40
10.40	10.40	10.20	10.50
10.40	10.40	10.20	10.60
10.40	10.40	10.20	10.65
10.45	10.35	10.25	10.70

[a] Volume of 0.005M zephiramine solution spent in titration, ml. 10ml of aqueous samples was titrated.

titration of anionic surfactant.

Initial volume fluctuations of the aqueous layer (10-25 ml) and the organic layer (7-15 ml) have no influence on the determination of the titration end-point. Table I shows the effect of concentration of the titrant on the titration of sodium lauryl sulfate.

The proposed method was applied to the determination of anionic surfactants such as sodium laurylbenzene sulfonate and Aerosol OT (di-2-ethylhexyl sodium sulfossucinate), in the same way as for sodium lauryl sulfate. Table II shows a comparison of the proposed method with two-phase dye transfer methods. The accuracy on the proposed method is + 0.5% or better from Table II. Sodium oleate did not give a sharp end-point in any range of concentration and caused positive errors in excess of the maximum permissible amount of 0.001 M. It is reasonable to consider that the complex formed between tetrabromophenolphthalein ethyl ester and quaternary ammonium ion is more stable than the carboxylic acid type surfactant-quaternary ammonium complex.

The effect of several salts on the titration of 10 ml of 0.005 M sodium lauryl sulfate indicated that the following ions did not interfere at the 0.001 M level: NH_4^+, K^+, Na^+, Ca^{++}, Mg^{++}, NO_3^-, $SO_4^=$, $CO_3^=$, acetate, citrate, Br^-, $C1^-$, and I^-.

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