Turbidimetric Analysis of Amine Oxides and Amine Oxide-Anionic Surfactant Mixtures

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ABSTRACT: Automatic turbidimetric analysis has been shown to be a simple and accurate method to determine the actives in anionic surfactants as well as the actives in amine oxides. This technique has been applied to dilute solutions of these surfactants in the μM range. Solutions containing mixtures of anionic surfactants and amine oxides can be positively resolved by turbidimetric titration without interferences. Performing two titrations at different pH values ensures that the amine oxide is completely in its nonionic form or totally protonated and behaving as a cationic surfactant.
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KEY WORDS: Amine oxides, anionic surfactants, turbidimetric analysis.

Simple analytical methods are available to analyze most single surfactants. These methods are widely used in production and quality control. The analysis of mixtures of surfactants is more difficult, however, and sometimes requires specialized techniques. The availability of simple analytical methods to determine quantitatively different surfactant species is important, both in surfactant research and in practice. Many formulations are mixtures of surface-active agents because of the performance advantage that results (1).

Many methods have been developed to analyze anionic and cationic surfactants. Today, considerable attention is being paid to the use of selective ion electrodes but, until now, a standard method based on this technique had not been developed. The most frequently used analytical method to determine actives in anionic and cationic surfactants is the two-phase mixed-indicator titration method (2–4). This method, developed as an improvement over the two-phase Epton titration method (5,6) is based on the different colors of the anionic surfactant/cationic dye and cationic surfactant/anionic dye salt complex that are soluble in the chloroform layer.

The previously mentioned analytical method is based on the aggregation phenomena of surfactant ions with other oppositely charged surfactant ions or dyes. The aggregation can be used directly for analysis of ionic surfactants by turbidimetric method. Hellsten (7) described a turbidimetric method in which chloroform is emulsified by the anionic surfactant to be titrated. With addition of cationic surfactant, the stability of the emulsion increases, thus varying optical density. At the equivalence point, the emulsion breaks rapidly. The maximum point in optical density vs. titrator volume curve is taken as the endpoint. Seguran (8) proposed a similar method: the colloidal precipitate, formed by the anionic surfactant being titrated by a cationic surfactant, is solubilized in the chloroform phase as it appears. Close to the equivalence point, solubility in the chloroform phase declines, and the aqueous phase hazes, producing a sudden fall transmittance that corresponds to the equivalence point. Fowler *et al.* (9) applied similar techniques to carry out sodium dodecylbenzene sulfonate (SDBS) determinations.

Park *et al.* (10) described turbidimetric and/or nephelometric methods that are also based on the aggregation phenomena of surfactant ions with other oppositely charged surfactant ions. One-phase turbidimetric titration of anionic surfactants has also been described (11), but the presence of nonionic surfactants and inorganic salts at high concentrations interferes with endpoint determination. Turbidimetric methods have also been applied to study mixtures of cationic polymers and anionic mixed micelles (12) and to analysis of polyacrylamides in the presence of sulfonates (13). No attention, however, has been paid to the turbidimetric analysis of surfactant mixtures, particularly those of anionic-amphoteric or anionic–amine oxide systems. Amine oxides behave like amphoteric surfactants in many cases. A turbidimetric technique was used by one of the authors to determine very low concentrations of these surfactants in mixtures, monitoring their diffusion through a collagen film (14–16). The object of this paper is to describe this turbidimetric procedure for analysis of anionic surfactant/amine oxide surfactant mixtures. It is simple, inexpensive, and easy to use. It is also applicable to the diffusion of mixtures that contain betaines.

EXPERIMENTAL PROCEDURES

Anionic surfactants. Sodium dodecyl sulfate (SDS) (Carlo Erba Reagenti; Milan, Italy) was reagent-grade, purity 92.63%. Purity was determined by International Standards Organization (ISO) 2271 (2). Sodium lauryl ether (2EO) sul-

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fate (LES), 27% active matter, was obtained from Tenneco España S.A. (Albright & Wilson Group). Active matter was determined by ISO 2271 (2). SDBS was reagent-grade, purity 81.09%. Active matter was determined by ISO 2271 (2). The following alkyl dimethyl amine oxides were all prepared by Albright & Wilson Ltd. (Oldbury, United Kingdom): decyl dimethyl amine oxide ($C_{10}AO$), 30.6% active; dodecyl dimethyl amine oxide ($C_{12}AO$), 30.2% active; tetradecyl dimethyl amine oxide ($C_{14}AO$), 28.8% active. Dodecyltetradecyl dimethyl amine oxide ($C_{1214}AO$), 30% active, was from Tenneco Españo S.A. (Albright & Wilson Group). Purities were determined by two-phase methylene blue indicator titration with SDBS in acid media.

Apparatus. The analysis of surfactants was carried out in a Radiometer TTT 80 automatic titrator with a Phototrode Mettler DP660 turbidometer (Mettler-Toledo S.A.E., Buchs, Switzerland). The turbidometer operates by detecting change in light transmission through a stirred solution.

Analysis of alkyl dimethyl amine oxides. A known volume of about 10 mL of sample is introduced in the titration vessel; 0.5 mL chloroform and 10 mL buffer solution at pH 2 (sodium citrate/HCl) (17) are then added. The vessel is placed in the automatic titrator, and its contents are stirred for a few minutes to achieve a uniform droplet size. Then the sample is automatically titrated against 4×10^{-3} M standard SDS solution at 25°C. The endpoint is detected at maximum turbidity.

Analysis of anionic surfactants. Analysis of anionic surfactants is performed in the same way as for alkyl dimethyl amine oxides but, in this case, the solution is buffered at pH 10 (sodium borate/NaOH) (16). The sample is automatically titrated against standard 4×10^{-3} M Hyamine 1622 solution (Merck, Darmstadt, Germany). The endpoint is detected at maximum turbidity.

Analysis of surfactant mixtures. Surfactant mixtures are analyzed by the procedure previously described, in two steps. First, a sample is analyzed for the anionic surfactant at pH 10 by titration against standard Hyamine solution. The amine oxide does not interfere at this pH. In a second step, a new sample is analyzed for the amine oxide. Two procedures are used, depending on whether the amine oxide exists in excess. When the molar amount of anionic surfactant exceeds that of amine oxide, the sample solution is buffered at pH 2 and then is titrated against standard Hyamine solution. The difference between the first and second titrations corresponds to amine oxide content. When the molar amount of amine oxide exceeds that of anionic surfactant, amine oxide can be titrated against standard SDS solution at pH 2, and the result is added to the result of the first titration. Alternatively, a back-titration procedure can be used. In this case, a known excess of standard SDS solution is added to the sample and buffered at pH 2. Amine oxide neutralizes the equivalent amount of SDS, and SDS excess is titrated against standard Hyamine solution. Again, amine oxide content is given by the amount of anionic surfactant previously determined plus the excess of anionic surfactant minus the result of titration with Hyamine solution.

RESULTS AND DISCUSSION

Alkyl dimethyl amine oxides behave as nonionic surfactants in alkaline media and as cationic surfactants in strong acid media. At any particular pH, amine oxide is in equilibrium with its protonated form

$$C_{12}AOH^{+} \Leftrightarrow C_{12}AO + H^{+} \qquad [1]$$

When anionic surfactant is added to a solution of amine oxide at low pH, precipitation occurs as follows:

$$C_{12}AOH^{+} + An^{-} \Leftrightarrow C_{12}AOH^{+} \cdot An^{-} \qquad [2]$$

where An^{-} is the anionic group of anionic surfactant. The overall reaction is obtained by combining the two equations as follows:

$$C_{12}AO + An^{-} + H^{+} \Leftrightarrow C_{12}AOH^{+} \cdot An^{-} \qquad [3]$$

The equilibrium constant for Equation 1 was found to be $K_a = 10^{-4.90}$, and the solubility product for Equation 2, when anionic surfactant is SDBS, was determined to be $K_{sp} = 10^{-10.8}$ (18). At pH 1, 99.98% of amine oxide is protonated. At pH 2, amine oxide is still completely protonated (99.87%). At pH 10, however, only 0.00079% exists in the cationic form. Then, at pH 2, the amount of amine oxide in the solution is negligible and, from Equations 1–3, amine oxide will precipitate quantitatively with anionic surfactant. Conversely, at an alkaline pH, the amount of protonated amine oxide is negligible and does not interact with anionic surfactant. Amine oxides are nonionic surfactants at neutral and alkaline pH. They are true cationic surfactants at a pH value below 3, and a mixture of both forms exists at intermediate pH values. Because pH 2 is enough to completely protonate the amine oxide, it was taken as the pH value for the analysis, thus avoiding possible hydrolysis of anionic surfactant.

The different behaviors of amine oxides and carboxy betaines simplify the analytical method. Betaines cannot exist as anionic surfactants because of the quaternary nitrogen, but they do behave as cationics in acid media. Because the pK_a of carboxy betaines is 1.8 (19), however, much lower than that of amine oxides, they protonate completely only under extremely acidic conditions. For example, at pH 2, only 38.7% is protonated. This makes analysis of betaines more difficult and requires turbidimetric titrations to be carried out at pH below 1. It is therefore advisable to titrate betaine by back-titration after addition of a known aliquot of an anionic (15,16).

During titration with anionic or cationic surfactant, the titrant first forms a finely divided precipitate, solubilized in chloroform. The contents of the reaction vessel are turbid and milky white in appearance. As titration progresses, turbidity becomes constant. Further titration disperses the precipitate, and the turbidity slowly decreases. The endpoint is read as the intersection of the two tangent lines to the titration curve. A titration curve is shown in Figure 1.

It was hypothesized (9) that the response of the phototrode is dominated by light scattered back from the droplets of chlo-

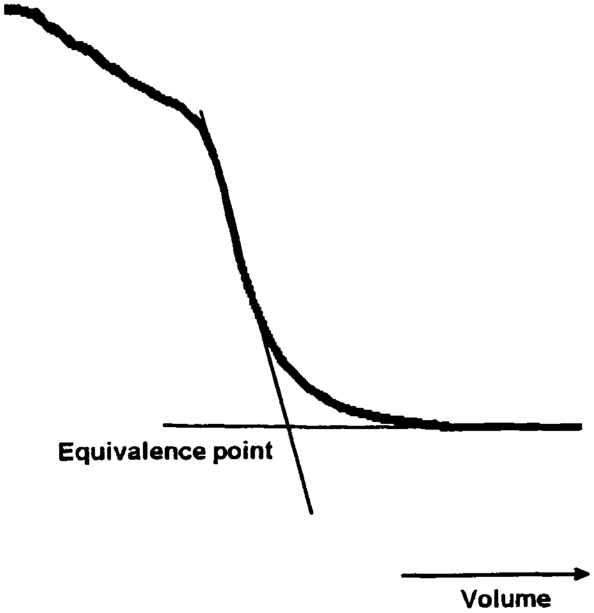

FIG. 1. General form of titration curves.

TABLE 1
Calibration Results for Sodium Dodecyl Sulfate (SDS) and $C_{1214}OA$[a]

Concentration (mM)			
SDS		$C_{1214}OA$	
Real	Found	Real	Found
0.1052	0.1072	0.05	0.040
	0.1072		0.039
0.16	0.1662		0.043
	0.1662		0.041
0.263	0.280	0.495	0.47
	0.240		0.49
	0.275		0.50
1.05	0.999		0.50
	1.058	0.99	0.97
	1.030		0.99
1.58	1.53		0.96
	1.53		1.00
2.63	2.63	4.9	5.1
	2.63		4.8
10.52	10.40		4.8
	10.51	9.9	9.8
15.78	15.53		9.8
	15.92	14.9	14.3
26.3	26.15		14.6
	26.54		14.6
		24.9	24.6
			24.2
			24.1

[a] Dodecyltetradecyl dimethyl amine oxide.

roform. Chloroform droplet size decreases as the interfacial tension between the aqueous and chloroform phases decreases due to the presence of active surfactant. As the endpoint is approached, the amount of active matter decreases, resulting in an increase in droplet size. Consequently, the transmittance decreases.

Linearity and precision of calibration curves. The method was tested on all surfactants (SDS, LES, SDBS, $C_{10}AO$, $C_{12}AO$, $C_{14}AO$, and $C_{1214}AO$). Calibration curves were obtained for each surfactant. Several different solutions of each surfactant were tested. Concentrations ranged from 0.1 mM up to 20 mM. Repeated titrations were made for each solution of SDS and $C_{1214}AO$ to allow the estimation of pure error, while all other surfactants were titrated only once at different concentrations. Results for SDS and $C_{1214}AO$ are shown in Table 1.

Calibration straight lines were adjusted by least squares, and their validity was checked at the 95% statistical level. The slopes, and the tabulated values of Fisher's F for $\alpha = 0.05$ and the F values found, are shown in Table 2. F_{exp} values, taking into account pure error when applicable, indicate that the hypothesis of linearity can be accepted. The slopes are close to unity, thus indicating the validity of the method. This excellent linearity is shown in Figures 2 and 3, which show the lines for SDS and $C_{12}AO$.

Because one of the most interesting aspects of this method is its sensitivity at low concentrations, it was applied to analyze several solutions at concentrations in the μM range. The standard error, using the calibration curve, is minimum for the mean value and increases as the value of the observation approaches the extremes. Confidence limits for SDS in the μM range for a single observation are ±260 μM and decrease as the number of replications increases. Consequently, it is advisable to analyze dilute samples with repeat determinations to minimize error. Average values are shown in Table 3. Relative errors ranged from 0.1 to 3.0%, with the exception of one relative error of 6.3%. This high error was obtained only in one of the many analyzes performed and was probably due to operating conditions in this particular series.

Analysis of surfactant mixtures. Analysis of surfactant mixtures was tested on two systems, SDS/$C_{12}AO$ and SDBS/$C_{12}AO$. Mixtures with known amounts of anionic (SDS, SDBS) and $C_{12}AO$ surfactants were prepared and titrated at different pH values by using suitable buffer solutions. The average results obtained for several mixtures of SDS/$C_{12}AO$ and SDBS/$C_{12}AO$ are shown in Table 4.

TABLE 2
Calibration Lines and Statistical Tests[a]

Surfactant	Slope	F_{exp}	$F_{0.95}$
SDS	1.000	0.21[b]	2.95
SDBS	1.011	29,466.1	7.71
LES	0.979	18,471.6	5.59
$C_{10}AO$	0.950	5,319.3	7.71
$C_{12}AO$	1.015	30,702.2	4.85
$C_{14}AO$	0.998	30,405.0	7.71
$C_{1214}AO$	0.977	0.85[b]	2.74

[a] Abbreviations as in Table 1; SDBS, sodium dodecylbenzene sulfate; $C_{10}AO$, decyl dimethyl amine oxide; $C_{12}AO$, dodecyl dimethyl amine oxide; $C_{14}AO$, tetradecyl dimethyl amine oxide.
[b] Evaluated through pure error.

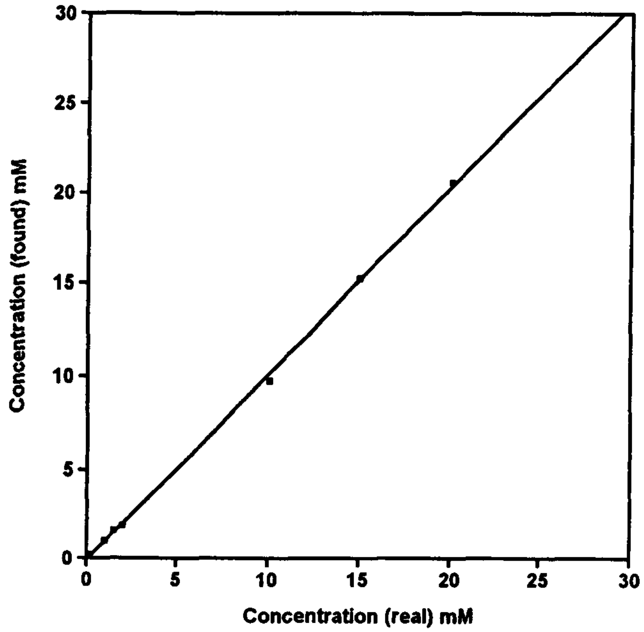

FIG. 2. Calibration straightline for sodium dodecyl sulfate.

When surfactants were mixed together, no gross interference was observed. The relative errors obtained were similar to those found for analysis of solutions containing single surfactants. The precision of the determination can be improved by increasing the number of replicated observations.

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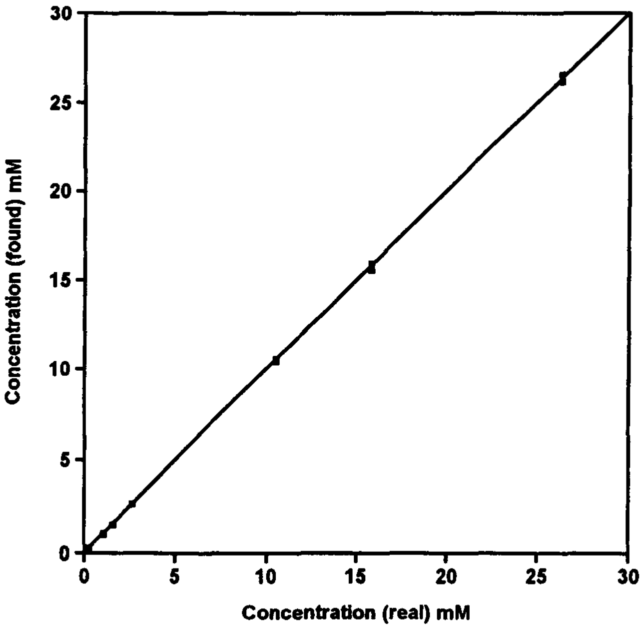

FIG. 3. Calibration straightline for $C_{12}AO$.

TABLE 3
Comparison Between Real and Found Surfactant Concentrations in Single-Surfactant Analyses[a]

	Concentration (μM)		
Surfactant	Real	Found	Error (%)
SDS	105.0	107.0	1.9
LES	40.0	40.8	0.2
SDBS	123.0	120.0	2.4
$C_{10}AO$	170.0	169.0	0.6
$C_{12}AO$	30.0	29.9	0.3
$C_{14}AO$	51.43	48.21	6.3
$C_{1214}AO$	39.6	40.7	2.8

[a]Abbreviations as in Tables 1 and 2.

TABLE 4
Comparison Between Real and Found Surfactant Concentrations in Surfactant Mixture Analyses[a]

Concentration (mM)					
Real		Found		Error (%)	
SDS	$C_{12}AO$	SDS	$C_{12}AO$	SDS	$C_{12}AO$
19.73	5.10	19.95	5.53	1.1	8.4
13.20	10.13	13.20	10.64	0.0	5.0
6.16	15.19	6.12	15.18	0.6	0.07
SDBS	$C_{12}AO$	SDBS	$C_{12}AO$	SDBS	$C_{12}AO$
18.47	5.06	18.37	5.02	0.5	0.8
12.32	10.13	12.05	9.58	2.2	5.4
6.15	15.19	6.32	15.19	2.8	0.0

[a]Abbreviations as in Tables 1 and 2.

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