

Application of an All-solid-state Ion-selective Electrode for the Automated Titration of Anionic Surfactants*

Salvador Alegret, Julián Alonso, Jordi Bartrolí, Jordi Baró-Romà, Joan Sànchez and Manuel del Valle†

Grup de Sensors & Biosensors, Departament de Química, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Catalonia, Spain

A poly(vinyl chloride) matrix membrane electrode responsive to anionic surfactants in an all-solid-state graphite-epoxy support was applied to the determination of anionic surfactants by potentiometric titration, using Hyamine 1622 as the titrant, in a pH 2.2 phosphate buffer. The results from this method compare favourably with those of the two-phase mixed indicator titration method for several commercial anionic surfactants (alkylsulfates, alkylbenzenesulfonates, α -alkene sulfonates, alkyl ether sulfates and sulfosuccinates). The performance characteristics improve the commercially available surfactant electrodes: the standard deviation for the titration of 4 mmol dm⁻³ dodecylsulfate with 4 mmol dm⁻³ titrant is 0.15% ($n = 23$), the relative standard deviation of the end-point potential is 0.95% and the average value of the potential jump is 140 mV, which allows for the titration of surfactants at concentrations down to 10 μ mol dm⁻³ and shows its applicability in routine analysis.

Keywords: Anionic surfactant determination; surfactant-selective electrode; potentiometric titration; poly(vinyl chloride) membrane electrode.

Introduction

When ionic surfactants are determined in environmental samples, they are usually determined using extraction-photometric procedures¹ that permit their evaluation at the sub-micromolar level. For industrial routine analysis, the usual procedure is the two-phase titration method² that can be carried out with reduced laboratory requirements and permits their determination at concentration levels greater than 0.1 mmol l⁻¹. However, this procedure presents several drawbacks, such as the difficult detection of the end-point, the time-consuming separation of phases between additions, especially for slow-reacting surfactants, and the use of hazardous solvents.

Ion-selective electrodes sensitive to ionic surfactants are of increasing interest for their use as end-point indicators, as there is no need for an organic solvent and because the procedure can be easily automated. The use of specially constructed electrodes for the potentiometric titration of surfactants has been reported previously, including poly(vinyl chloride) membrane electrodes³⁻⁷ and coated-wire electrodes.⁸ Other electrodes not specifically constructed for surfactant response have also been employed successfully for their determination, such as the fluoroborate electrode.^{7,9} Although the more widely used surfactants are the anionic groups, the use of ion-selective electrodes has also been extended to the determination of cationic and zwitterionic

surfactants,^{3,10} and to the non-ionic type.^{11,12} Efforts have also been made in order to incorporate these electrodes in flow systems, in order to perform automated flow pseudo-titrations of ionic surfactants.^{3,13} Recently, two different surfactant electrodes^{14,15} have been commercialized, facilitating the determination of detergents in non-specialized laboratories.

This paper reports the application of a specially constructed all-solid-state PVC-membrane surfactant electrode¹⁶ for the potentiometric titration of a large variety of commercial anionic surfactants, comparing the results obtained with those given by the standard two-phase titration procedure. The anionic surfactants evaluated were alkylsulfates, alkylbenzenesulfonates, α -alkene sulfonates, alkyl ether sulfates, sulfosuccinates and alkylphenol polyglycol ether sulfates.

Experimental

Reagents

All reagents used for the preparation of the membranes and working solutions were of analytical-reagent grade. Standard and reagent solutions were prepared using doubly-distilled water. The cationic surfactants Hyamine 1622 (Merck) and cetyltrimethylammonium bromide (Panreac, Barcelona) were tested as titrant solutions. Standard solutions of anionic surfactants were prepared with sodium dodecylbenzenesulfonate (DBS) (Carlo Erba) and sodium dodecylsulfate (DS) (Fluka). Mixed indicator for the two-phase titration method was prepared using didymium bromide (Panreac) and Disulfine Blue VN150 (Merck).² Buffer solutions used in the potentiometric titration were pH 3.0 citrate buffer and pH 2.2 phosphate buffer, both 0.5 mol dm⁻³ in total concentration. Surfactants used in the comparison study were sodium dodecylbenzenesulfonate, triethanolamine dodecylsulfate, α -alkene sulfonate, sodium dodecyl ether sulfate, obtained from Molins Kao (Barcelona), and ammonium dodecylsulfate, triethanolamine dodecylsulfate, sodium dodecyl ether sulfate, sodium 2-ethylhexylsulfate, diisooctyl sulfosuccinate, polyethoxylated fatty alcohol sulfosuccinate, ethoxylated dodecyl alcohol sulfosuccinate and sodium alkylphenol polyglycol ether sulfate, obtained from Witco España (Barcelona).

Equipment

The all-solid-state PVC membrane surfactant electrode^{17,18} was constructed as described previously;¹⁶ the composition of the membrane was 12.5% m/m ion-pair complex (quaternary ammonium salt of dodecylbenzenesulfonate), 25% m/m of high relative molecular mass poly(vinyl chloride) (Fluka) and 62.5% m/m of *o*-nitrophenyl octyl ether (Fluka). After use, the electrode was rinsed with doubly-distilled water and stored in air. Titrations were performed with the aid of an automatic

* Presented at The International Symposium on Electroanalysis (A Tribute to J. D. R. Thomas), Cardiff, Wales, UK, April 6-8, 1994.

† To whom correspondence should be addressed.

titrator constructed in the laboratory from an automatic burette (Crison microBUR 2030) equipped with a 10 ml syringe (Hamilton), a digital potentiometer equipped with a serial RS-232 interface (Crison micropH 2002), and a personal computer, which permitted 40 mm³ minimum volume additions. The titration cell was furnished with a magnetic stirrer, the surfactant electrode and the reference electrode (an Orion 90-02 double liquid junction Ag–AgCl reference electrode with 1 mol dm⁻³ potassium sulfate solution in the salt bridge). Software for the titrations with variable-volume additions was written in QuickBasic. End-point volumes were calculated from derivative treatment of the data.

Procedure

For the titration, an adequate volume of the sample was taken, 1 ml of pH 2.2 phosphate buffer was added, the electrodes were immersed in the cell and the potential was recorded for different volumes of 4 mmol dm⁻³ Hyamine 1622 titrant once it had stabilized to ± 0.5 mV. The titration speed could be up to 0.8 ml min⁻¹. The two-phase titration method was performed following the standard mixed-indicator procedure.²

Results and Discussion

Response Characteristics

The response characteristics of the constructed electrode¹⁶ are summarized in Table 1. The calibration parameters correspond to an ionic medium of 0.166 mol dm⁻³ K₂SO₄ + 0.01 mol dm⁻³ trisodium citrate, with the pH adjusted to 4.00 with sulfuric acid. These data correspond to the mean of twelve calibration runs, carried out with three electrode units during 4 months, in which alternate calibrations with DBS and DS were made. The random variations observed during this period did not show any significant trend that could suggest wear of the membrane.

The response times indicated in Table 1 were evaluated by recording the changes of potential when a concentration step from 0 to 10⁻⁴ mol dm⁻³ was made, and calculating the time necessary to reach 90% of the final steady value. The values presented correspond to the mean of several experiments during 2 months, and did not show any alteration during the period considered. Despite the long response times found, which are caused by the decreased mobilities of the voluminous surfactant ions in water, acceptable readings can be made with fixed delay times shorter than 2 min. It is noteworthy that

Table 1 Response characteristics of the constructed PVC-membrane electrodes sensitive to anionic surfactants. Values presented for each surfactant are mean values of 12 calibration runs with three electrode units during 4 months. The calibration parameters correspond to the equation $E = E^\circ - m \log(\text{activity})$, where $m = \text{slope}$

Surfactant	Parameter	Value
DBS	E°	75.1 \pm 2.1 mV
	Slope	38.6 \pm 2.7 mV per decade
	Correlation coefficient	>0.9992 ($n = 5$)
	Limit of detection	6 \times 10 ⁻⁶ mol dm ⁻³
	Response time	4.6 min*
DS	E°	120.1 \pm 1.7 mV
	Slope	45.0 \pm 5.5 mV per decade
	Correlation coefficient	>0.9983 ($n = 5$)
	Limit of detection	4 \times 10 ⁻⁶ mol dm ⁻³
	Response time	3.2 min*

* Calculated as the time required to attain the 90% of the final steady value for a concentration change from 0 to 10⁻⁴ mol dm⁻³.

the response times are increased, mainly owing to the slow reaching of the final 15% e.m.f. value, as observed on the transient response recordings.¹⁶ These response-time values are also comparable to the values found with commercial surfactant electrodes.

The selectivity characteristics of the developed membrane, evaluated following the mixed solutions method¹⁹ by different calibrations using DBS as primary ion, showed that common ions such as chloride and sulfate did not interfere significantly. When different anionic surfactants are treated as interferents, they present selectivity coefficients close to unity, indicating a general response behaviour to the different anionic surfactants.

Potentiometric Titrations

Although cetyltrimethylammonium bromide (CTA) proved acceptable as a titrant, Hyamine 1622 was preferred, as it can be obtained in a high-purity grade, is more stable and because of the higher end-point potential breaks observed. End-point breaks for the titration of 4 mmol dm⁻³ standard sodium dodecylsulfate solution were about 150 mV with Hyamine 1622 and about 100 mV with CTA solution, both with a 4 mmol dm⁻³ titrant concentration.

The reverse titration of cationic surfactants with standard sodium dodecylsulfate is also feasible, as the electrode shows a Nernstian response to cationic surfactants in the 10⁻⁵–10⁻² mol dm⁻³ range, as has also been observed with other PVC-membrane electrodes.⁴

The developed electrode permitted the titrations to be carried out in the pH range 2–12.¹⁶ The pH finally selected for

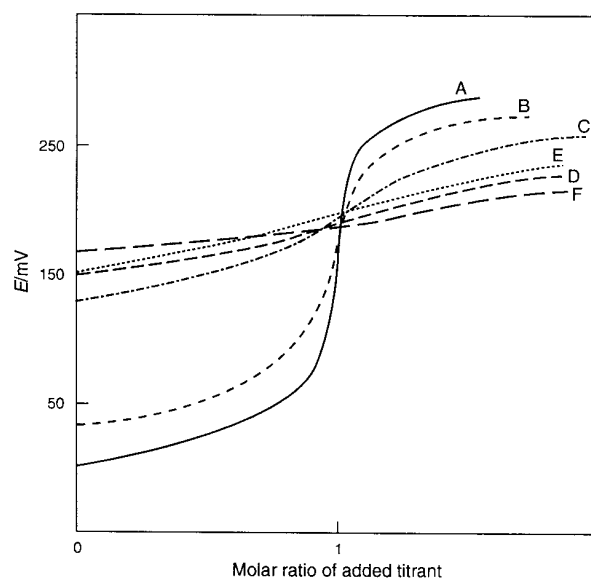


Fig. 1 Titration plots at different concentration levels of surfactant and titrant, showing the applicability of the titration procedure down to the 10⁻⁵ mol dm⁻³ level of surfactant concentration.

	Surfactant concentration/ mol dm ⁻³	Titrant concentration/ mol dm ⁻³
A	2.5 \times 10 ⁻³	4 \times 10 ⁻³
B	2.5 \times 10 ⁻⁴	4 \times 10 ⁻³
C	4 \times 10 ⁻⁵	1 \times 10 ⁻³
D	2.5 \times 10 ⁻⁵	4 \times 10 ⁻³
E	2 \times 10 ⁻⁵	1 \times 10 ⁻³
F	2 \times 10 ⁻⁵	1 \times 10 ⁻⁴

the titrations was highly acidic in order to resemble the conditions of the standard procedure.² Moreover, titration in acidic medium can be used to differentiate mixtures of soaps and surfactants.^{2,20} For this purpose, a pH 3.0 citrate buffer and a pH 2.2 phosphate buffer were evaluated. The pH 2.2 phosphate buffer was selected as it yielded better titration curves, probably owing to the different hysteresis effect with the two media.

Fig. 1 shows the potentiometric-titration curves obtained when the concentrations of anionic surfactant, standard sodium dodecylsulfate solution, and the titrant are diminished in order to establish the minimum determinable concentration. Solutions down to the 10^{-5} mol dm⁻³ level can be determined when the titrant solution used is 4 mmol dm⁻³. The end-point break under these conditions is approximately 30 mV and the sigmoidal curve is still well recognized.

Application

In order to carry out an extensive comparative study of the results yielded by the titrations using the constructed electrode, different types of anionic surfactants found in the detergent industry were determined by both the potentiometric titration and the standard procedure. Potentiometric determinations were repeated four times and the standard titrations were performed in triplicate. Table 2 presents the results obtained for the different samples used in this comparative study. The set of surfactants tested comprised the alkylsulfate, alkylbenzenesulfonate, α -alkene sulfonate, alkyl ether sulfate and sulfosuccinate types. Using the potentiometric procedure, all the titration curves had the expected sigmoidal shape for the set of detergents tested. With samples ranging from 3% to 99% m/m active matter, the pooled standard deviations (s , absolute value) are 0.49% m/m for the

standard two-phase titration and 0.17% m/m for the potentiometric titration. Table 3 presents two statistical treatments of the comparative study of the two procedures, showing an excellent agreement at the 95% confidence level.

The results for the surfactant sodium 2-ethylhexylsulfate were not included in the comparison, as its titration with the standard two-phase mixed-indicator procedure presents several problems related to the short length of the alkyl chain moiety.² For its determination, a different indicator (Methylene Blue) was used in the standard titration. Nevertheless, when titrated potentiometrically, it gave acceptable curves but with smaller end-point breaks than for long alkyl chain surfactants. The results for the considered sample, with this alteration in the procedure, were 36.3% m/m active matter and relative standard deviation (s_r) of 1.1% with the batch titration, and 38.7% m/m active matter and s_r of 0.3% for the potentiometric titration.

Other surfactants also tested were sodium alkylphenol polyglycol ether sulfates, which showed poor agreement of the results between the two methods. This is caused by the dual behaviour of this group of surfactants, which present both anionic and non-ionic characteristics, and need larger reaction times for their titration. Hence, the differences can be justified by the different times employed for each titrant addition between the manual two-phase titration and the automated potentiometric titration. These discrepancies could be solved using special conditions for the potentiometric titration, such as a slow rate of addition of titrant.

For the developed surfactant electrode, three different titration runs of 10 cm³ of standard 4 mmol dm⁻³ sodium dodecylsulfate titrated with 4 mmol l⁻¹ Hyamine 1622 were performed on three different days, in order to evaluate the reproducibility of the results. Table 4 gives a statistical summary of each of the titration series, including the means

Table 2 Comparison between the results of the standard two-phase titration method (quadruplicate) and potentiometric titration (triplicate) with the developed electrode in the determination of different anionic surfactant types

Surfactant (sample No.)	Standard two-phase titration		Potentiometric titration	
	Active matter (% m/m)	s (%)	Active matter (% m/m)	s (%)
α -Alkene sulfonate	39.9	1.2	40.0	2.7
Sodium dodecylbenzenesulfonate	98.8	0.8	99.8	0.5
Ammonium dodecylsulfate (1)	26.1	0.6	25.9	0.9
Ammonium dodecylsulfate (2)	24.3	0	26.6	0.6
Sodium dodecyl ether sulfate (1)	28.5	0.5	28.3	0.6
Sodium dodecyl ether sulfate (2)	20.1	3.8	19.9	1.7
Sodium dodecyl ether sulfate (3)	71.7	0.7	71.5	0.8
Triethanolamine dodecylsulfate (1)	41.4	0.6	41.6	0.2
Triethanolamine dodecylsulfate (2)	42.5	1.8	42.5	0.3
Triethanolamine dodecylsulfate (3)	40.0	2.5	40.6	1.6
Polyethoxylated fatty alcohol sulfosuccinate	3.1	0	2.7	0
Ethoxylated dodecyl alcohol sulfosuccinate	31.0	0.8	33.5	1.0
Diisooctyl sulfosuccinate	67.5	0.6	68.8	0.4
Sodium dodecylsulfate (1)	28.8	0	29.1	0
Sodium dodecylsulfate (2)	29.5	0.5	29.5	0.8

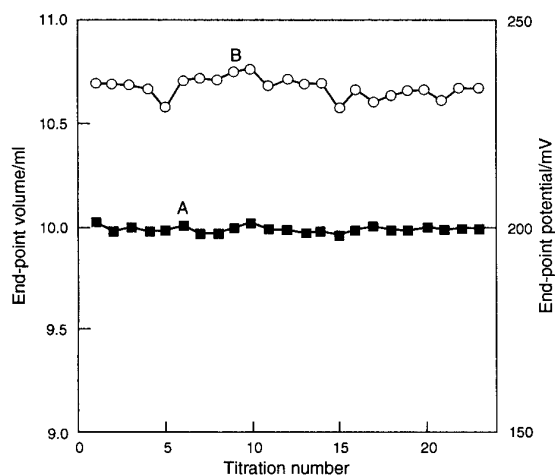
Table 3 Statistical treatments in the comparison of the standard two-phase titration and the potentiometric titration methods for the determination of surfactant content in different surfactant samples: linear regression and Student's paired t -test

Linear regression	Standard <i>versus</i> potentiometric Potentiometric <i>versus</i> Standard (correlation coefficient = 0.99929, $n = 15$)	Slope = 1.006 ± 0.023 Slope = 0.992 ± 0.022	Intercept = 0.2 ± 1.0 Intercept = -0.1 ± 1.0
Student's t -test	t (calculated) = 2.006	t (tabulated)* = 2.145	

* Tabulated value at the 95% confidence level.

Table 4 Statistical summary of the results obtained in the reproducibility study of the titration of the 4 mmol dm⁻³ sodium dodecylsulfate standard solution

Titration series	No. of samples	Mean end-volume/cm ³	s _r (%)	Mean end-potential/mV	s _r (%)	End-point break (90/110%)/mV
I	21	9.865	0.14	234.6	0.70	145.5
II	21	9.855	0.17	229.4	0.95	144.4
III	23	9.983	0.14	233.7	1.1	140.8

**Fig. 2** Reproducibility of the titration results for the replicate determination of 4 mmol dm⁻³ dodecylsulfate: A, end-point volume and B, end-point potential.

for the end-volume, the end-point potential and the end-point potential break. This end-point break was calculated as the difference of the interpolated potentials at an added titrant molar ratio of 110% and 90%, respectively. The values for the end-volume are highly reproducible within each series, with a pooled s_r of 0.15%. Differences found between the different series correspond to the different sodium dodecylsulfate solutions used. Although it was possible to perform the titrations up to a fixed potential owing to the high reproducibility of the end-point potential read (the pooled s_r was 0.95%), the titrations were always completed with an excess of titrant, in order to obtain the complete titration curve. Fig. 2 shows the end-point volumes and potentials for one of the series, for which a single equivalent point was detected in all instances. Concerning the shape of the titration curves, the values found for the end-point breaks were unexpectedly large, 140 mV, greater than other values reported in the literature for similar conditions,⁷ which allowed us to determine low concentrations of surfactants. The large potential breaks may be explained by the combined electrode response to both anionic and cationic species. The data for the commercial electrodes under the same titration conditions⁷ are s_r for the end-point potential of 2% and 0.66%, and end-point breaks of 60 and 67 mV for the Orion and Metrohm electrodes, respectively. When the titration curves corresponding to one of these series are superimposed, almost a unique trace is seen, indicating negligible wear of the PVC-membrane electrode during a day's work. The constructed electrodes have been in discontinuous use for 2 years, showing the robustness of the design and the excellent characteristics of the developed PVC membrane. During the various studies carried out, no reconditioning of the electrodes was necessary.

Conclusions

The performance of the constructed electrodes is excellent, both with regard to response characteristics and when used as end-point indicators in potentiometric titrations of several types of anionic surfactants normally found in the detergent industry, and they show good agreement with the standard two-phase titration results. The reproducibility of the end-point potential and the large end-point breaks improve the performance of commercially available electrodes.

We thank D. Montlló, of Witco España, for her help and valuable comments. Part of the application work was carried out by C. Fortuny, supported by CIRIT (Generalitat de Catalunya).

References

- 1 *Standard Methods for the Examination of Waters and Wastewaters*, American Public Health Association, Washington, DC, 15th edn., 1980, pp. 530–532.
- 2 Heinerth, E., in *Anionic Surfactants. Chemical Analysis*, ed. Cross, J., Marcel Dekker, New York, 1977, ch. 6.
- 3 Birch, B. J., and Cockcroft, R. N., *Ion-Sel. Electrode Rev.*, 1981, **3**, 1.
- 4 Dilley, G. C., *Analyst*, 1980, **105**, 713.
- 5 Dowle, C. J., Cooksey, B. G., Ottaway, J. M., and Campbell, W. C., *Analyst*, 1987, **112**, 1299.
- 6 Zelenka, L., Sak-Bosnar, M., Marek, N., and Kovacs, B., *Anal. Lett.*, 1989, **22**, 2791.
- 7 Buschmann, N., and Schulz, R., *Tenside Surfactants Deterg.*, 1993, **30**, 18.
- 8 Vytras, K., *Electroanalysis*, 1991, **3**, 343.
- 9 Selig, W., *Fresenius' Z. Anal. Chem.*, 1980, **300**, 183.
- 10 Buschmann, N., and Schulz, R., *Tenside Surfactants Deterg.*, 1992, **29**, 128.
- 11 Jones, D. L., Moody, G. J., Thomas, J. D. R., and Birch, B. J., *Analyst*, 1981, **106**, 974.
- 12 Gallegos, R. D., *Analyst*, 1993, **118**, 1137.
- 13 Dowle, C. J., Cooksey, B. G., Ottaway, J. M., and Campbell, W. C., *Analyst*, 1988, **113**, 117.
- 14 Tehrani, M., and Thomae, M., *Am. Lab.*, 1991, **23**, No. 19, 8.
- 15 *Application Bulletin*, 1993, No. 233/1 e, Metrohm, Herisau.
- 16 Baró-Romà, J., Sánchez, J., del Valle, M., Alonso, J., and Bartrolí, J., *Sens. Actuators B*, 1993, **15–16**, 179.
- 17 Lima, J. L. F. C., and Machado, A. A. S. C., *Analyst*, 1986, **111**, 799.
- 18 Alegret, S., and Florido, A., *Analyst*, 1991, **116**, 473.
- 19 Cragg, A., Moody, G. J., and Thomas, J. D. R., *J. Chem. Educ.*, 1974, **51**, 541.
- 20 Anghel, D. F., and Ciocan, N., *Anal. Lett.*, 1977, **10**, 423.

Paper 4/02837F
Received May 13, 1994
Accepted July 18, 1994

J. Alonso, J. Baró, J. Bartrolí, J. Sánchez, M. del Valle. "Flow-through tubular ion-selective electrodes responsive to anionic surfactants for flow-injection analysis". *Anal. Chim. Acta*, **308**, 115-121 (1995)

Abstract

Es descriu un sistema d'injecció en flux amb detecció potenciomètrica dissenyat per a la monitorització del contingut en tensioactius aniónics en solucions de rentat de planxes d'impressió. Per a aquesta aplicació són emprats dos nous elèctrodes selectius amb membrana de PVC, construïts amb un disseny tubular per a treball en flux sense la incorporació d'una solució interna de referència. La mostra, que presenta una elevada força iònica i un pH extremadament bàsic, és pretractada i condicionada en un sistema de flux bicanal, permetent la determinació de tensioactiu dins de l'interval situat entre 1×10^{-4} i 1×10^{-3} M, en medis molt salins i agressius que poden presentar una concentració de NaOH que pot arribar a 0.3 M.