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Flow-through tubular ion-selective electrodes responsive to anionic surfactants for flow-injection analysis

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Abstract

A flow-injection system based on potentiometric detection and designed for the monitoring of anionic surfactant content of printing plates washing solutions is described. Two new PVC membrane ion-selective electrodes, constructed with an all-solid-state tubular flow-through design, are used. The sample, with high ionic strength and extremely alkaline pH, is conditioned in a two-channel flow-injection system, allowing for surfactant determination in the 1×10^{-4} to 1×10^{-3} M range, with NaOH contents up to 0.3 M.

Keywords: Flow system; Ion selective electrodes; Printing plates

1. Introduction

Anionic surfactants comprise a large group of synthetic substances with multiple uses in the industrial and domestic field. Their wide consumption makes relevant their determination during the manufacturing steps or at environmental level. The routine procedure for the industrial control of detergents is based on a two-phase titration [1], but it has several drawbacks, namely it is time-consuming, uses hazardous solvents, and lacks automation possibilities.

The development of electrodes sensitive to anionic surfactants represents an attractive alternative, normally using the potentiometric titration technique, to these analytical determinations, and with added advantages of easy automation, reduction of the determination time to a few minutes, a lower consumption of reagents and higher precision in the determination of the end-point. Recently, these surfactant electrodes have been introduced commercially [2,3], facilitating surfactant determination in non-specialized laboratories.

In previous work, the development of all-solid state PVC membrane electrodes sensitive to anionic surfactants [4] was presented. This paper introduces the use of the developed membranes in tubular flow-through electrodes for flow-injection systems. In this way, the determination of anionic detergents becomes very fast and reproducible, thanks to the implicit advantages of the flow technique.

Flow-injection systems have been applied to a large variety of fields, but there are few publications concerning the determination of surfactants. Normally the described systems use liquid–liquid extraction, with spectrophotometric detection [5,6] or

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atomic absorption spectrometry [7]. A flow-injection system with tensammetric detection has also been described for the determination of surfactants [8]. The use of potentiometric detection has only been used by Dowle et al. [9], who performed flow pseudotitrations with specially developed tubular graphite electrodes, internally cast with a PVC membrane.

The present work shows the applicability of the developed tubular sensors in flow-injection systems for the determination of anionic surfactants by direct potentiometry. The application for the determination of Teepol (a commercial surfactant composed of a mixture of alkylsulphates) in printing plates washing solutions, with high saline content and extremely alkaline pH (NaOH content 0.2 M) is described.

2. Experimental

2.1. Reagents and equipment

All reagents used were of analytical reagent grade, and all solutions were prepared using doubly distilled water. Stock surfactant solutions, dodecylbenzenesulphonate (DBS) and dodecylsulphate (DS), were stored at 5°C to minimize their degradation. The Teepol HB7 solutions (Shell Industrial Chemicals, London) were standardized by potentiometric titration with Hyamine 1622.

The flow system used employed a 4-channel peristaltic pump (Gilson Minipuls 2), a motorized injection valve (Hamilton HVLX6-6), and PTFE tubing (0.7 mm bore). Potentiometric measurements were made with a digital potentiometer ISE Amplifier (MBT Environmental, Barcelona). As reference electrode, a double liquid junction Ag/AgCl electrode (Orion 90-02) with a 1 M potassium sulphate solution in the salt bridge was used. Adaptors for the reference electrode and stabilizing devices have been previously described [10]. A first manifold with computer data acquisition, shown in Fig. 1a, was used to study the working conditions. A two-channel flow system, used for sample conditioning in the surfactant determination in printing plates washing solutions, is also shown in Fig. 1b. For the latter, the carrier solution was 5×10^{-6} M sodium dodecylbenzenesulphonate, and its flow rate 1.34 ml min^{-1}. The conditioning solution was potassium sulphate with a 0.2 M ionic strength, and its pH adjusted to 2.5 with concentrated sulphuric acid. The conditioning solution flow rate was 0.87 ml min^{-1}.

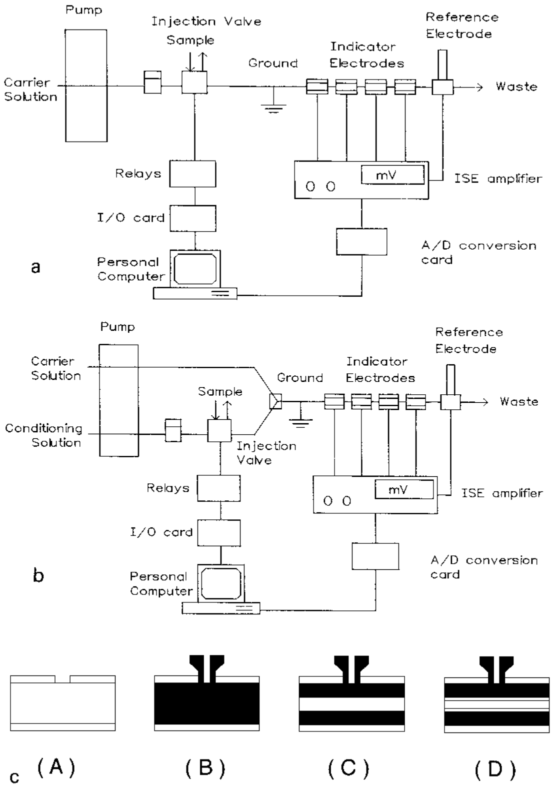

Fig. 1. (a) Manifold for the study of the response characteristics. (b) Manifold for the determination of surfactant content in printing plates washing solutions. Injected volume, 20 μl; Carrier solution, 5.0×10^{-6} M DBS; flow rate, 1.34 ml min^{-1}; conditioning solution, K_2SO_4 ($I = 0.2$ M), pH 2.5; flow rate, 0.87 ml min^{-1}. (c) Construction of the flow-through tubular ion selective electrodes. (A) Perspex tube, (B) casting of the conductive resin, (C) drilling, (D) casting of the PVC membrane.

2.2. Preparation of the PVC membrane electrodes

The different sensing membranes were prepared (in weight) with 25% high molecular weight polyvinylchloride (PVC) (Fluka), 62.5% *o*-nitrophenyloctyl ether (Fluka), and 12.5% ion pair complex (quaternary ammonium salt of dodecylbenzenesulphonate). The ion pair complexes were prepared by mixing 0.1 M aqueous solutions of the different soluble salts, and the obtained complex was separated, dried, and recrystallized from a suitable organic solvent. Two different membranes were tested, their differences relating to the nature of the quaternary ammonium salt used [4]. Fig. 1c outlines the design and construction procedure of the all-solid-state tubular flow-through electrodes sensitive to anionic surfactants [11,12]. A Perspex cylinder with an electrical contact is filled with the conductive support (an epoxy resin–graphite powder mixture). After curing, a 1.5 mm width inner channel is drilled longitudinally, and the PVC membrane cast on the inner wall of the support.

3. Results and discussion

3.1. Study of the characteristics of response

Some intrinsic response characteristics of the developed sensors, such as their pH dependence, selectivity characteristics and response times, have previously been described for electrodes with a conventional potentiometric configuration [2].

Using a flow system, these intrinsic characteristics are preserved, but as the sample is inserted into a carrier solution, this must be optimized in composition. First, it is desirable to incorporate a small amount of primary ion, in order to quickly recover the baseline values after the injection of sample, although this background level can modify the linear range of response. Using a surfactant background level of 1×10^{-6} M of DBS, the return-to-baseline times varied from 2 to 8 min with the highest concentration surfactant standard, 10^{-2} M. A background level of 5×10^{-6} M DBS permitted recovery times below 2 min in all cases.

Further, the carrier solution needs to incorporate an inert salt to give the necessary electrical conductivity to the flow system. A high saline level is required to buffer the ionic strength of the samples. The saline composition of the carrier solution influences the response rate of the electrodes, and the upper limit of linear response, modifying the critical micelle concentration value for the surfactant tested. The type of salt used also defines the minimum determinable concentration and lowers the calibration slope, due to its interference effect. Avoiding lipophilic interfering anions, different salts as chloride, hydrogenphosphate and sulphate were assayed as carrier solutions. The results are presented in Table 1. Chloride shows the more stable baselines but with large recovery times, due to the interference effect; this salt presented a narrower linear range and the smallest sensitivity. Hydrogenphosphate showed several advantages, good sensitivity and an ample linear calibration range, but the baseline tended to drift considerably. Sulphate gives the best saline composition, with a compromise of the different desirable characteristics, with good linearity, good calibration characteristics and lower detection limits.

When the ionic strength is lowered, larger linear working ranges are obtained; at lower concentrations of surfactant the interference effect is diminished, while at the higher range the critical micelle concentration break is observed at larger concentration values. In this way, the ionic strength preferred is 0.01 M, and it was not further lowered so as to retain some buffer capacity.

Next, the different variables of the flow system were studied. Augmenting the injected volume of sample, an increase of the measured signal up to a stable value for injected volumes greater than 300 μl is verified. Fig. 2 shows the effect of the injected volume for a low surfactant concentration standard, with three different carrier solutions, also pointing out the influence of the salt used, as discussed above.

The flow rate employed influences the perfor-

Table 1
Calibration parameters obtained with DBS, using different carrier solutions

Salt used in the carrier solution	$I = 0.1$ M			$I = 0.01$ M		
	E^0 (mV)	s (mV/dec.)	Corr. coeff.	E^0 (mV)	s (mV/dec.)	Corr.coeff.
NH_4Cl	239.1	46.1	0.9989	298.9	58.0	0.9995
K_2HPO_4	264.0	51.4	0.9877	309.9	61.0	0.9995
K_2SO_4	277.6	52.6	0.9977	293.3	57.0	0.9999

Calibration equation: $E = E^0 + s \cdot \log(\text{DBS activity})$. Injected volume of sample, 250 μl.

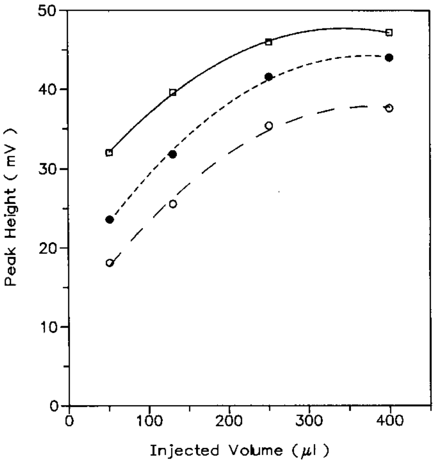

Fig. 2. Effect of the injected volume on the peak height of a 5×10^{-5} M DBS standard with different carrier solutions. Flow rate, 2.5 ml min^{-1}. (□) K_2SO_4, $I = 0.1$ M; (●) K_2HPO_4, $I = 0.1$ M; (○) NH_4Cl, $I = 0.1$ M.

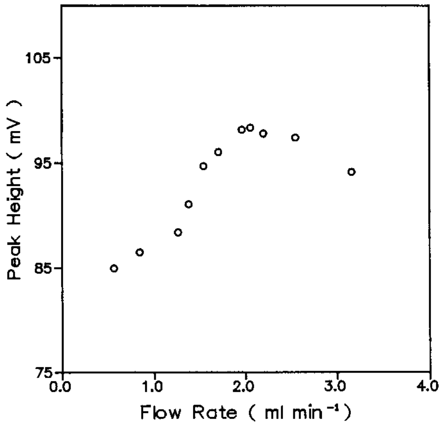

Fig. 3. Variation of the measured signal with the flow rate, from an injection of 100 μl of a 5.0×10^{-4} M DBS standard.

mance of the flow system, mainly in the measured signal and in the return-to-baseline times, which in turn determines the sampling rate. Fig. 3 shows the variation of the measured signal with increasing flow rate, where a maximum can be observed. The increasing zone of the curve at lower flow rates corresponds to the samples that have suffered more dispersion before arriving to the detector. At the same time, the transport rate of analyte through the stagnant layer close to the electrode is low. When the flow rate is increased, the width of this layer is reduced, and the analyte reaches the sensing membrane readily, increasing the response rate of the sensing device. With the higher flow rates, the time available for the sample to reach the membrane through the stagnant layer is lowered, being less than the intrinsic response time of the electrode, thus decreasing the measured signal. On account of these phenomena, a maximum response is obtained for this sensor around 2 ml min^{-1}. Concerning the recovery times after an injection, Fig. 4 shows the cleaning effect at the electrode surface when the flow rate is increased.

The optimized characteristics of the flow system are summarized in Table 2, with the observed recovery times for the concentration range 10^{-5}–10^{-2} M of DBS. Fig. 5 shows a typical calibration run with four electrode units in series, employing dodecylsulphate (DS) as the analyte.

One of the main advantages of the constructed electrode is the general response behaviour to different anionic surfactants, which permits the global determination of this group of substances. Table 3 shows the calibration results with three different surfactants, DBS, DS and Teepol HB7. The first tested membrane presents larger slopes, better linearity and lower detection limits, so is recommended in the case studied. Membrane II yields better results only with samples with a high surfactant concentration, as it gives better linearity at this calibration range. The difference between membranes I and II is the quaternary ammonium salt used for the prepara-

Table 2
Characteristics of the optimized flow-injection system

Ionic strength	0.01 M
Carrier solution composition	3.33×10^{-3} M K_2SO_4 + 5.0×10^{-6} M DBS
Flow rate	2.5 ml/min
Injected volume	100 μl
Return-to-baseline time	0.3–0.8 min

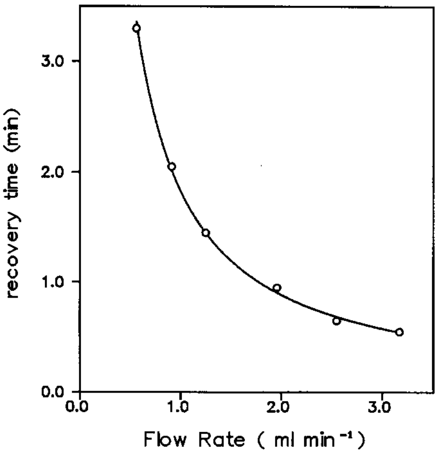

Fig. 4. Effect of the flow rate on the return-to-baseline time, with an injection of 100 μl of a 5.0×10^{-4} M DBS standard.

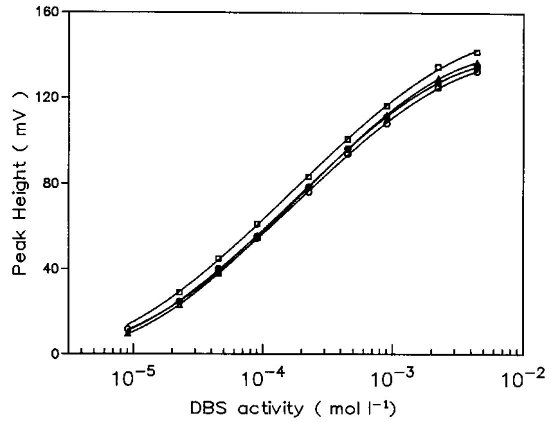

Fig. 5. Calibration graph of four electrode units employed in series, with DS standards. Carrier solution K_2SO_4 ($I = 0.01$ M) + DBS 5.0×10^{-6} M; injected volume, 100 μl; flow rate, 2.5 ml min^{-1}. (○) Unit 1; (●) unit 2; (□) unit 3; (△) unit 4.

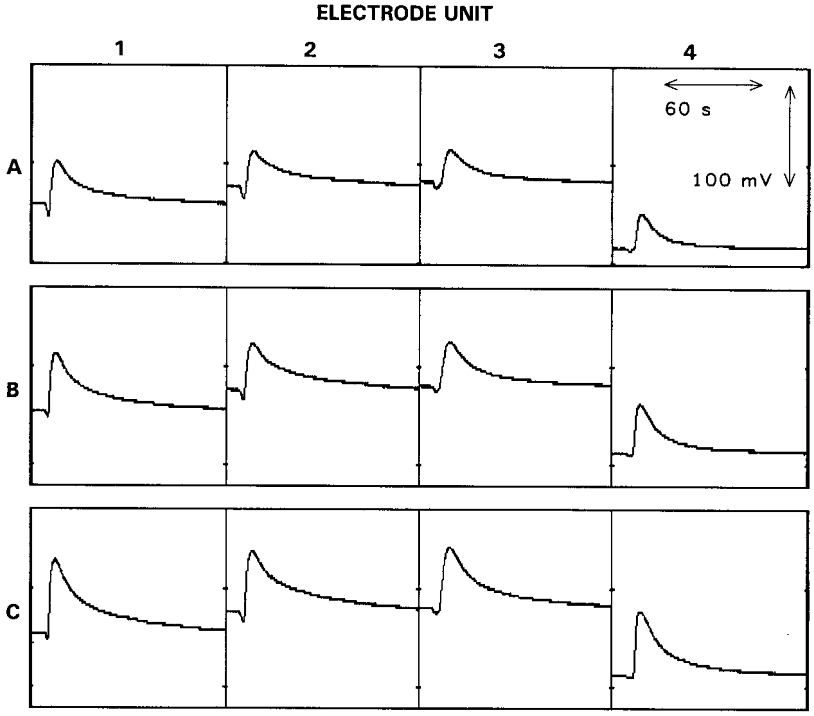

Fig. 6. Peaks obtained during the determination of surfactant content in printing plates washing solutions with four electrode units in series. (A) [Teepol] = 2.5×10^{-4} M, [NaOH] = 0.2 M; (B) [Teepol] = 5.0×10^{-4} M, [NaOH] = 0.2 M; (C) [Teepol] = 1.0×10^{-3} M, [NaOH] = 0.2 M.

Table 3
Summary of the response characteristics of the constructed electrodes to different surfactants

Surfactant	Parameter	Membrane I	Membrane II
DBS	E^o (mV)	292.0 (4.5)	274.8 (13.5)
	s (mV/dec.)	59.6 (4.6)	55.1 (14.2)
	Linear range (log c)	−3.3/−4.3	−3.3/−4.3
	Detection limit (log c)	−4.91 (1.5)	−4.99 (1.0)
	Corr. coeff., $n = 6$	> 0.9997	> 0.998
DS	E^o (mV)	279.7 (2.4)	244.5 (9.7)
	s (mV/dec.)	54.8 (2.6)	49.4 (8.1)
	Linear range (log c)	−3.0/−4.6	−2.4/−4.0
	Detection limit (log c)	−5.10 (1.1)	−4.95 (2.3)
	Corr. coeff., $n = 6$	> 0.9996	> 0.9996
Teepol	E^o (mV)	232.9 (5.0)	191.7 (14.0)
	s (mV/dec.)	46.6 (6.5)	40.9 (13.6)
	Linear range (log c)	−3.0/−4.3	−2.4/−4.0
	Detection limit (log c)	−5.00 (2.6)	−4.69 (2.8)
	Corr. coeff., $n = 6$	> 0.997	> 0.998

Values in parentheses correspond to standard deviations obtained (%R.S.D.).

tion of the ion pair complex, tetradodecylammonium and Hyamine 1622, respectively.

3.2. Application

The determination of surfactant content in washing solutions for printing plates of the print industry is important in certain applications where these must be kept strictly clean. These cleaning solutions are formulated with 2×10^{-4} M of surfactant (Teepol HB7), high saline content and extremely alkaline pH (NaOH content 0.2 M).

The previously described flow system is well suited to the surfactant content of the sample, but it will present interference effects due to the high saline content and to the extreme pH. The two-channel flow-injection system was used instead, in which the sample could be readily conditioned. In it, a smaller volume of sample (20 μl) was injected in a water carrier solution with a background level of surfactant, and mixed with the conditioning and buffer solution before arriving to the detection system, where the flow-rate and other conditions are similar to those found previously. The recording of the potential obtained with four identical electrode units placed in series, with three injections of simulated samples, is shown in Fig. 6, with results comparable to those previously obtained. In this case, the peak heights are smaller as are the detection limits, this fact caused by the dilution effect of the two-channel manifold. Although Fig. 6 shows different absolute values of potential for electrode 4, the analytical signal, the peak height, is maintained constant. From the figure, the utility of the measuring scheme is noticed, where it is possible to perform sequential determinations with different tubular electrodes placed in series, as the distortion of the injected sample plug when passing through these detectors is minimized.

Table 4
Mean errors found in the determination of samples simulating printing plates washing solutions

Electrode unit	[NaOH], mol l^{-1}	Mean error (%)	Overall mean error (%)
1	0.1	4.2	
	0.2	13.6 [a]	4.1
	0.3	3.9	
2	0.1	1.8	
	0.2	2.4	2.5
	0.3	3.2	
3	0.1	4.9	
	0.2	3.9	5.1
	0.3	6.7	
4	0.1	0.9	
	0.2	0.9	0.9
	0.3	1.3 [a]	

The values correspond to the mean (absolute value) obtained for three surfactant concentrations: 1.0×10^{-4} M, 2.5×10^{-4} M, 5.0×10^{-4} M Teepol HB7.

[a] Values rejected according to Dixon's Q test at the 90% confidence level.

A simulation study of the determination of surfactant content of printing plates washing solutions was performed varying the NaOH content between 0.1 and 0.3 M, and with surfactant content between 1×10^{-4} and 5×10^{-4} M. Table 4 shows the mean errors between the found and the real values for three surfactant concentrations, showing a good concordance and without being significantly influenced with the NaOH content. Errors of approximately 1% may be obtained, as shown with electrode unit 4, that would correspond to a mixing coil of ca. 50 cm. The sample throughput achieved is around 30 samples per hour.

4. Conclusions

The use of flow-injection potentiometry for the direct determination of surfactants presents great advantages when compared with standard two-phase titration procedures, namely a high sample throughput, good reproducibility and the use of very simple and non-hazardous solutions. From a basic flow-injection set of conditions, the manifold can be easily adapted to different industrial monitoring situations by simple changes considering the characteristics of the samples.

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Abstract

Es descriu l’aplicació de membranes selectives a anions tensioactius, basades en matrius optimitzades de policlorur de vinil, a sensors ISFET. Els dispositius desenvolupats han mostrat un temps de vida superior als quatre mesos, millorant els valors publicats per a altres ISFETs de membrana de PVC. És de destacar l’obtenció de pendents nernstians, compresos entre 59 i 62 mV/dècada, límits de detecció situats al voltant de 10^{-6} M i una bona linealitat. La resposta tant a diferents espècies tensioactives com al reactiu emprat en la valoració potenciomètrica, fa possible la determinació del contingut global en anions tensioactius presents en diferents mostres. A més de les característiques bàsiques de les membranes, es mostra els resultats corresponents a les valoracions potenciomètriques sobre mostres conegudes emprant els ISFETs preparats. Els dispositius poden ser emprats en el rang comprès entre 0.02 i 10 mM per a solucions de dodecilbenzesulfonat, obtenint salts de potencial de fins a 250 mV en les valoracions. La reproductibilitat, avaluada a partir de solucions patró 4mM de dodecilsulfat de sodi, va ser del 1.45 % (n = 14), expressada com a desviació estàndard relativa. Finalment, en un estudi comparatiu, no van ser trobades diferències significatives entre els resultats obtinguts pel mètode estàndard de la valoració en dues fases i el mètode proposat, que empra els ISFETs de tensioactius com a indicadors de punt final.