Surfactants Analysis from Natural Waters Using Nonfaradaic Processes

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Voltammetric measurements of dissolved surface-active substances in aqueous solutions, as specific commercial detergents, are described in the present paper. Two voltammetric methods based on the adsorption phenomena at mercury electrode/aqueous solution interface were performed in order to obtain the analytical signal for the detergent analysis. The first method was direct current polarography (DC), based on the suppression of polarographic maxima of mercury (II) and the second method was the alternative-current polarography (AC)-the tensammetric method. Both methods are very sensitive, allowing to determine the traces of surface active substances in aquatic media, but the tensammetric method has the advantage to be easier to carry out for surfactants determinations. In order to evaluate the content of surfactants in the analysed water samples, the TRITON-X-100 equivalent values obtained have been correlated with the concentration of the detergents in water samples. Both proposed methods allow to determine the content of the surfactants in very low concentration and have been applied on real water samples.

Keywords: surfactants, natural waters, pollution, voltammetry, tensammetry

Surfactants are organic compounds that are able to effect or change the surface of a material and are wide used in many industries, such as soaps, cosmetics, textiles, paint and detergents. In the same time, they are the most common waters pollutants, being considered an indicator of the water pollution level. Due to this fact, the surfactants have recently attracted big interest from protection environmental agencies and consequently much attention have been payed to the analytical methods for the determination of these dangerous substances. Among the analytical methods used to determine the content of surface-active substances, the electrochemical techniques are one of the most suitable for the investigation of surface-active substances [1-6]. Therefore, different electrochemical techniques have been used to investigate the surface-active substances: cyclic voltammetry, potentiometry, amperometry, tensammetry, electrocapillary measurements, direct current polarography based on the interpretation of polarographic maximum of mercury (I), or on the interpretation of polarographic maximum of mercury (II) [1-5] and biosensors [6,7].

Among electrochemical methods, those based on the adsorption of the surface-active substances represent sensible, simple and non-destructive methods to study adsorbable organic compounds [8,9]. These substances exhibit surface activity, reflected by their adsorption at the solution-electrode interface. The mentioned process forms the basis for direct determination of the adsorbable molecules by specific techniques of voltammetric methods in alternating current (AC), known as “tensammetry”. The AC voltammetric methods show the particular property of being applicable not only to electron-transfer reactions (faradaic processes), but also for the electroinactive compounds analysis . In this case, the response (current – voltage curve or the tensammetric curve) reflects the changes of the differential capacity of the double-layer with the potential due to the adsorption-desorption processes involving the analyte, which take part in the electrode/solution interface (nonfaradaic processes).

The tensammetric curves have analytical utility and are used to extend the electroanalytical methods to molecules and ions which are not electroactive: detergents, petroleum fractions, vitamins, dyestuffs, enzymes, pesticides, proteins, sugars, organic polymers [2-5].

Nonfaradaic processes may also be investigated by some other electroanalytical methods as, for example, electrocapillary measurements, suppression of the polarographic maxima and measurement of the charging current [8,9].

The continuous increase of surface-active consumption increases also the risk of the environment pollution due to their release in natural waters. Even if most of the surface-active compounds are biodegradable, their accumulation or the accumulation of their biodegradation products in natural waters can affect the natural growth of aquatic flora and fauna. Therefore, much research activity is focused on the development of new fast, reliable analytical methods (spectrophotometric, chromatographic, electrochemical methods) for water quality control, from the surfactants content point of view [10,11].

This paper reports the analytical applications of two electrochemical methods for the measuring of the concentration of surface-active substance in solution of some commercial detergents: a method based on suppression of the second polarographic maxima and a tensammetric method.

Experimental part

The experimental techniques used to evidence the nonfaradaic processes induced by the studied surface-active compounds were the direct- and alternating-current polarography. The alternating current polarography was used with an amplitude of the signal of 10 mV and the

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Table 1

EFFECT OF DIFFERENT EXPERIMENTAL PARAMETERS UPON THE Hg (II) POLAROGRAPHY MAXIMA CURRENT

Effect of support electrolyte concentration		Effect of surface-active substance concentration*	
KCl, M	i, μA	Triton X-100, μg/l	i, μA
2	2.73	0	3.27
1	3.07	25	1.77
0.5	1.23	50	0.68
0.1	0.20	75	0.34

*At 1M KCl

frequency 60 Hz. The instrument employed for the mentioned techniques was a Radelkis OH-105 polarograph.

The electrochemical cell consists from a dropping mercury electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a silver wire as counter electrode. The characteristics of the dropping mercury electrode measured in bidistilled water at 0.0 V versus SCE and at a mercury column height of 65 cm were the following: dropping time, t_1=1.94 sec and mercury flow rate, m = 8.9 mg/s.

All the reagents used were of analytical purity grade (Merck). The support electrolyte was either 0.1 M KCl for the tensammetric measurements or 1 M KCl for the experiments based on suppression of the polarographic maxima. KCl was purified by recristalisation, in order to prevent the perturbation of the polarographic maxima due to the traces of the organic mater from the reagent. As a model surfactant was used Triton X-100. Fresh three-time distilled water was used to prepare the necessary solutions.

The detergents under study were commercial products purchased from the store and here are not presented with their real denominations, being further denoted by D1, D2, D3 and D4. The detergent solutions were prepared by dissolving an accurate weight amount of detergent in pure water. All experiments were performed at 20 ± 1 °C, maintaining the temperature using a thermostat device. The dissolved oxygen removal was achieved by purging the sample with pure argon gas for 10 min.

Results and discussions

Suppression of polarographic maxima

This method is based on the suppression effect by the surface-active component on the second kind of the polarographic maxima occurring on the polarographic reduction wave of the Hg(II) ion. This effect was compared with that produced by a model surface-active compound, Triton X-100.

In order to record well-developed second maxima of mercury, the polarographic experiments have to be performed in some specific conditions, such as a high mercury flow rate, concentrated solutions of supporting electrolyte, and a high degree of purity of the distilled water, of the reagents and of the laboratory environmental as well [8].

The experimental data presented in table 1 express the effect of support electrolyte concentration on the polarographic maxima current, and also the suppression effect of added surface-active compound. These parameters influence the formation of the Hg (II) polarographic maxima in the known way [9]. Further experiments were performed in 1 M KCl supporting electrolyte. The experimental results from table 1 evidences that the polarographic maxima are very sensitive to the presence of a surface-active compound, in this case the model surface-active compound Triton X-100.

The suppression effect on the second polarographic maxima in the presence of surface-active compounds makes possible to detect them at very low concentration (under 0.001 g/L). The calibration graph is built-up by plotting the height of the polarographic maximum as a function of the detergent concentration. As an exemple, figure 1 presents the influence of added detergent D3 on the Hg (II) second kind polarographic maxima current.

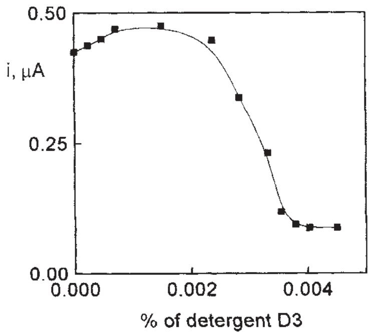

Fig.1. Dependence of the Hg(II) 10^{-3} M polarographic maxima current on the content of detergent D3. Electrolyte 1 M KCl

Unfortunately, the graph does not show a linear shape and, consequently, a very careful calibration is required. The shape of the graph can be explained by taking into account the complexity of the phenomena involved both in the formation of the polarographic maxima and in their suppression by adsorption of surface-active compounds on the mercury electrode surface. Besides, some practical problems are encountered due to the lack of selectivity of the polarographic maxima suppression and due to the difficulty to control all the experimental parameters that influences the formation of the polarographic maxima.

Similar graphs were obtained when one of the other detergent (D1, D2 or D4) was added into the solution.

Tensammetric determination of surface-active compounds

All the investigated detergents produced a tensammetric signal at the same potential, at -1.25 V vs. SCE (insertion in fig. 2).

This suggests that this method cannot discriminate between different type of surface active compounds, but from the standpoint of water quality control, such an information is not very important. On ther contrary, this should be an advantage because in this way the overall surfactant concentration can be evaluated as all of them take part in adsorbtion.

The calibration graphs for all the investigated detergents are presented in figure 2. The tensammetric peak height was measured toward the base line record at more

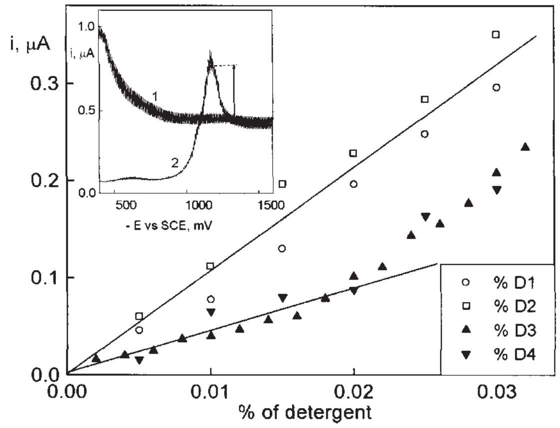

Fig. 2. Influence of the detergent concentration (mg in100 ml KCl 0.1 M) on the tensammetric peak current. To convert the x-axis scale in Triton X-100 equivalent content a multiplication factor of 3.85 has to be used for detergents D1 and D2, respectively 1.4 for detergents D3 and D4. Inset: the corresponding tensammetric record for a solution of KCl 0.1 M with: 0 (1); 0.046 % (2) detergent D2. The amplitude of the signal:10 mV. The frequency: 60 Hz

Table 2
THE DETERGENT CONTENT IN THE ANALYSED WATER SAMPLES

Water Sample	Detergent content %	Equivalent Triton X-100 concentration (mg/L) for (D1+D2)*	Equivalent Triton X-100 concentration (mg/L) for (D1+D2)**
1.	0.003	0.011	0.0042
2.	0.001	0.0038	0.0014
3.	0.004	0.0152	0.0056
4.	0.002	0.0076	0.0028
5.	0.005	0.0191	0.007
6.	0.001	0.0038	0.0014
7.	0.004	0.0152	0.0056

* Multiplication factor=3.85; ** Multiplication factor=1.4

negative potential, which has the same shape in the absence (curve 1, insertion fig. 2) or in the presence of the surface-active compound (curve 2, insertion fig. 2). Because the formation of this tensammetric signal is due to an adsorption-desorption process, the linearity of the calibration graph is restricted only to a relatively narrow range of concentration. By increasing the surface active compounds concentration in the sample, the graph tends to deviates from linearity, due to saturation of the mercury electrode surface with adsorbed molecules. This is not a major drawback provided that sample concentration will be adjusted by dilution to the favourable concentration values.

The chosen model compound, Triton X-100, exhibits a tensammetric signal at –1.55 V versus SCE. The calibration graph based on the correlation between the tensammetric current and the content of the surface-active compound shows a liniar correlation until a concentration of 2 mg/L Triton X-100. This calibration function allows us to translate the calibration graphs of the commercial detergents to a calibration graph relative to Triton X-100 content. Thus, for detergents D1 and D2, the x-axis of the calibration graph should be multiplied with 3.85, while for detergents D3 and D4 the multiplication factor is 1.4. It is important to mention that detergents D1 and D2, which are provided by the same manufacturer produce almost identical calibration graph. This suggest that the content of surface-active component from the detergent formulation is almost the same in both detergents. The same conclusion emerges for the group of detergents D3 and D4, produced by another manufacturer.

The determination of surfactants in water samples

The described tensammetric method was applied in the determination of detergent content from 7 water samples originated from Arges river near Bucharest at Rosu point, during the summer of 2007, in different days. The experimental data are presented in table 2 and show that in the analysed water samples the percentage of the total detergent (D1+D2+D3+D4) is less than 0.01%.

It may be assumed that the respective percentage is due to the detergents D1 and D2 and then the equivalent Triton X-100 concentration is less than 0.02 mg/L (using 3.85 as multiplication factor), or that the detergents are D3 and D4 and the detergent content in water sample is less than 0.007 mg/L (with 1.4 as multiplication factor). Taking into account both calculation ways, the obtained values demonstrated a very low level pollution with surfactants of water source samples.

Conclusions

Two methods to determine the surface-active compounds are presented. The first is the method using the second polarographic maxima of the Hg(II) and the second is the method using the tensammetric peak as analytical signal. Both methods, based on the adsorption of the surface-active substances on the surface mercury electrode allow to determine the content of these substances in water. Due to the fact that it is generally recognised that the tensioactive substances constitute a real danger for the environmental quality, their analyse is especially important. By comparing the two methods, it can be concluded that the second method is more adequate to analyse the traces of surfactants in natural waters.

The analysed water samples contain insignificant amount of surfactant, denoting that the water source under study is a non-polluted one from the standpoint of surfactant content for the tested period of time.

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