Research Article

Simple Electrochemical Determination of Surface-Active Substances in Natural Waters

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A simple electrochemical determination of surface-active substances by using time-dependent variation of the capacitive current in a.c. voltammetry at the HMDE is described. Surface-active substances were accumulated by stirring solution at the deposition potential of -0.6 V versus Ag/AgCl (sat. NaCl). The capacitive current was recorded for different deposition times in the range 0–120 s, wherefrom the linear calibration plot is constructed. The proposed method was verified for model surfactant TritonX-100 in the concentration range 0.02–0.25 mg/L and for humic acid in the concentration range 1.65–20 mg/L. The application of the method was demonstrated for freshwater samples of the Drava river, Danube river, and the wetland Kopački Rit, Croatia. The shape of the i_{ac} - E curves as well as the obtained concentrations of surface-active substances by using humic acid as the calibration substance are quite well describing the type and the nature of organic matter in the freshwater samples.

1. Introduction

Organic substances with surface-active properties represent a significant part of dissolved organic matter in natural aquatic systems [1, 2]. Those substances are either naturally present or products of man's activities. The latter are very often, especially in the case of commercial tensides, less abundant in mass while on the contrary they may represent the most surface-active organic material in a particular sample [2].

Although organic surface-active substances are usually electroinactive, that is, those chemical species do not undergo electroreduction or electrooxidation within the available potential window, they can be analyzed by electrochemical methods on the basis of their influence upon the electrode double-layer structure when they get adsorbed at the electrode surface. Surface-active substances were most extensively investigated by electrochemical methods in the sea [3–7], particularly in the thin layer at the sea surface [8–10], in estuarine [11], and river water systems [12, 13], and recently in the atmospheric precipitation samples [14]. Adsorption study at the electrode-solution interface may allow quantification of surface-active substances by measuring the extent of adsorption. In the case of a mixture

of adsorbable substances, the adsorption effect is expressed by using the convenient calibrating substance.

The application of the adsorption study for the analysis of organic surface-active substances has been developing in two main directions: (a) by introducing new or improvement of already existing techniques of measurement [15–17], (b) by using electrochemical method for molecular characterization of the complex mixture of naturally occurring organic adsorbable substances. The latter can be done through comparison of the electrochemical behaviour of the organic matter in the natural sample with the behaviour of the selected model substances and/or by using a complex methodological approach where different analytical techniques are combined with the electrochemical measurement [18, 19].

So far, a.c. voltammetry, particularly tensammetric method with adsorptive preconcentration based on recording either capacitive current or double layer capacity versus potential curves, has been most widely and successfully used for the determination of surface-active substances in aquatic systems. For quantification of the content of surface-active substances, a calibration plot of a selected standard is used, which is in fact the apparent adsorption isotherm for the selected substance at a selected accumulation time. Recently,

a quick and simple tensammetric method was proposed that makes use of a variation in the differential capacity of double layer in relation to the time of accumulation by means of the controlled growth mercury electrode (CGME) [16]. The application of the method was illustrated on two model substances and in the determination of surface-active substances of the river water samples.

While investigating the organic matter content and the chemical composition of real natural water samples, one has to be aware of the fact that the parameters of organic matter could be changed in time and during sample treatment. Therefore, it is a great advantage if one can use simple, direct, and nondestructive analytical methods, possible in the field work and/or on board of a ship. Here, we have used a simple, portable electrochemical instrument in field measurement of surface-active substances in the river water samples. The tensammetric method of determination is modified by means of the time-dependent variation of capacitive current at the HMDE wherefrom the calibration plot was constructed.

2. Experimental

Surface-active substances were analyzed electrochemically by a.c. voltammetry using PalmSens portable instrument (Palm Instruments BV, Netherlands). Three electrode system was used: hanging mercury drop electrode (HMDE WK 2, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland) as a working electrode, Ag/AgCl (sat. NaCl) as the reference electrode, and platinum wire as the counter electrode. The potential of $E = -0.6$ V was applied for accumulation of surface-active substances at different accumulation times with stirring. An applied alternating voltage of 10 mV and the frequency of 75 Hz were used. The measurements were carried out in a constant-temperature room at ambient temperature (293-+1 K) in the cell open to air, without any sample deaeration. Freshwater samples and model substances were analyzed by addition of sat. NaCl to obtain 0.55 mol/L NaCl solution.

For calibration, the nonionic surfactant polyethoxyethylene-t-octylphenol (Triton-X-100) from Rohm and Haas, Milan, Italy and humic acid from Aldrich (former EGA-Chemie), Germany were used. This is a peat humic acid of molecular weight distribution of two pronounced peaks, one for a molecular mass of 1000 Da and the other for 5000 Da as reported earlier [20].

Freshwater samples were collected from the Drava river near Osijek, Croatia and the Danube river near Batina at the state border between Croatia and Hungary, as well as in the wetland of the Kopački Rit, Croatia.

Dissolved organic carbon (DOC) content of the freshwater samples was determined by using a high-temperature catalytic oxidation analyzer (TOC-5000 Model, Shimadzu, Japan).

3. Results

3.1. Principles of Time-Dependent Tensammetric Determination. It is well known that in a stirred solution, a layer of

thickness δ (Nernst diffusion layer), in which no motion of the solution occurs, exists at the electrode. The concentration of electroactive species within this diffusion layer vary linearly with distance from the electrode [21]. Presuming a fast reaction, concentration of reactant on the electrode surface is practically zero.

In our investigations, the reactant is not a species undergoing a redox process but instead is adsorbed on the electrode. In the case of a strong adsorption and relatively short time, that is, low coverage of the electrode surface, the surface concentration of the surfactant, Γ , is defined as:

$$\Gamma = \frac{M}{A} = \frac{Dc_0t}{\delta}, \quad (1)$$

where M is number of moles of surfactant, A is the electrode area, D diffusion coefficient, c_0 bulk concentration of surfactant, and t adsorption time.

At a constant potential, differential capacity of the electrode double layer can be expressed as [22]:

$$C_d = C_{\Theta=0}(1 - \Theta) + C_{\Theta=1}\Theta, \quad (2)$$

where $C_{\Theta=0}$ is the differential capacity of a free electrode surface, $C_{\Theta=1}$ is the differential capacity on a completely covered surface and Θ is the relative surface coverage,

$$\Theta = \frac{\Gamma}{\Gamma_m}, \quad (3)$$

where Γ_m is Surface concentration at maximal coverage.

From (2) and (3):

$$C_d = C_{\Theta=0} - (C_{\Theta=0} - C_{\Theta=1})\frac{\Gamma}{\Gamma_m}, \quad (4)$$

$$C_d = C_{\Theta=0} - K_1\Gamma,$$

where K_1 is the constant since $C_{\Theta=0}$, $C_{\Theta=1}$, and Γ_m are constants for a given surfactant.

In the tensammetric measurements, C_d is proportional to a.c. current, i_{ac} , and therefore:

$$i_{ac} = K_2C_d = K_2(C_{\Theta=0} - K_1\Gamma). \quad (5)$$

From (5) and (1),

$$i_{ac} = K_2\left(C_{\Theta=0} - K_1\frac{Dc_0t}{\delta}\right). \quad (6)$$

With constant speed of solution stirring and surfactant concentration,

$$i_{ac} = K_2C_{\Theta=0} - K_3t, \quad (7)$$

where

$$K_3 = \frac{K_1K_2Dc_0}{\delta}. \quad (8)$$

Therefore, the dependence of a.c. current, i_{ac} , on time of deposition, t , is a straight line with negative slope and intercept on i_{ac} axis.

FIGURE 1: i_{ac} - E curves for (a) humic acid, 25.85 mg/L, and (b) Triton-X-100, 0.143 mg/L, recorded for increasing deposition times in 0.55 M NaCl solution. Deposition potential was -0.6 V, amplitude 10 mV, and frequency 75 Hz.

With higher concentrations of surfactants it might be more favourable to measure under diffusion conditions. Diffusion current can be expressed by Cottrell equation [23]

$$i_d = \frac{nFADc_0}{\sqrt{\pi Dt}}. \quad (9)$$

In order to develop the equation for the dependence of a.c. current on surfactant concentration, we start with (9) and proceed in the same manner as above. The final dependence of a.c. current on time is

$$i_{ac} = K_2 C_{\Theta=0} - K_3 \sqrt{t}, \quad (10)$$

where

$$K_3 = K_1 K_2 \frac{c_0 \sqrt{D}}{\sqrt{\pi}}. \quad (11)$$

Thus, under diffusion conditions, current is proportional to the square root of time of deposition.

3.2. Application of the Method: Model Substances and Natural Samples. In order to test our experimental conditions, two model surfactants were used, T-X-100 and humic acid. In Figures 1(a) and 1(b), the dependence of a.c. current on potential for the two surfactants are given. At the potential of -0.6 V, which is close to the potential of electrocapillary zero, both surfactants are strongly adsorbed. Decrease of i_{ac} with t was measured by registering i_{ac} at 0, 15, 30, and 60 s of deposition, each time on a fresh Hg drop, and with stirring of solution. A series of straight lines was obtained for T-X-100 and humic acid (Figures 2(a) and 2(b)) as expected from (7). It would have been more appropriate to measure continuously the change of current with time for

TABLE 1: Determination of surface-active substances in freshwater samples by electrochemical method. Concentrations are expressed in equivalent amounts of two different standards (Triton-X-100 and humic acid). Concentrations of dissolved organic carbon (DOC) in the samples are given too. Samples were collected and analyzed on March 3, 2006.

Freshwater samples	DOC mg C/L	SAS equiv. T-X-100, mg/L	SAS equiv. Humic a., mg/L
Drava River, Osijek	4.91	0.067	15.97
Danube River, Batina	4.21	0.079	18.78
Kopački Rit, Wetland	10.13	0.077	18.47

each concentration, but, unfortunately, the instrument used for the field measurements had no such possibilities.

Since field measurements are often done in a span of several days or even months and with different HMDE, the electrode surface areas could vary somewhat. In order to minimize such errors, the lines in Figure 2 were plotted as relative currents by dividing all values with the intercept of the line for supporting electrolyte, which was 0.55 mol L^{-1} NaCl (Figures 3(a) and 3(b)). Supporting electrolyte was recorded before every set of measurements.

For each surfactant, the relative slope K_3 of i_{ac} - t lines was plotted against bulk concentration of the surfactant. Good, straight lines, with intercept equal to zero, were obtained in both cases (Figures 4(a) and 4(b)). The concentrations of the mixture of the unknown surfactants from natural waters were always measured using these two calibration lines, that is, they were reported as equivalent to a certain concentration of T-X-100 and humic acid.

FIGURE 2: i_{ac} - t curves for different concentrations of (a) T-X-100: (1) 0 mgL^{-1} , (2) 0.0237 mgL^{-1} , (3) 0.0594 mgL^{-1} , (4) 0.0951 mgL^{-1} , (5) 0.143 mgL^{-1} , and (6) 0.190 mgL^{-1} and (b) humic acid: (1) 1.65 mgL^{-1} , (2) 4.4 mgL^{-1} , (3) 6.6 mgL^{-1} , (4) 10.45 mgL^{-1} , and (5) 16.5 mgL^{-1} . Supporting electrolyte: 0.55 M NaCl . Peak-to-peak amplitude 10 mV , frequency 75 Hz . Each point represents a freshly formed Hg drop.

FIGURE 3: i_{ac} (relative)- t curves obtained by dividing the results in Figure 2 by the value for supporting electrolyte at $t = 0 \text{ s}$.

The linear calibration plot represents an improvement of the tensammetric method in comparison with the use of the calibration plot which is the apparent adsorption isotherm for a selected model surfactant at one selected adsorption time. The calibration plot obtained at one selected accumulation time can be used only in a narrow

concentration range, that is, below surface saturation [5, 24]. When surface-active substances are determined in different aquatic samples, sometimes they need to be measured at different accumulation times in order to extend the concentration range. In comparison to the use of several adsorption isotherms, each for the selected accumulation

FIGURE 4: The calibration curves for (a) T-X-100 and (b) humic acid constructed by plotting the slopes from i_{ac} (relative)- t lines against concentrations. All conditions as in Figures 2 and 3.

FIGURE 5: i_{ac} - E curves for a sample of Drava river with increasing deposition times from 0 s (dotted line) to 120 s. Deposition potential was -0.6 V, amplitude 10 mV, frequency 75 Hz. 0.55 M NaCl was added to the sample.

FIGURE 6: $i_{ac}(\text{relative})$ - t curve constructed from the results in Figure 5. i_{ac} current was recorded at -0.6 V. The slope was calculated from the first 5 points on the curve.

time, the advantage of the proposed method is based on the fact that in the time-dependent variation of the capacitive current, all data for different accumulation times are used in one plot, and the concentration of surface-active substances is determined from the linear calibration plot.

The application of the method for the surfactant analysis in a natural water sample is illustrated in Figures 5 and 6.

In Figure 5 are given i_{ac} - E curves for a sample of Drava river in Croatia. Deposition was done at -0.6 V with stirring

of solution. From the shape of the curves, it follows that the surfactants present in that sample behave more like humic acid than T-X-100. No well-defined desorption peaks at negative potentials were observed as in the case of T-X-100. Instead, a low and extended hump around -1.2 V to -1.6 V suggests a partial desorption of segments in the surfactant molecule similar to humic acid. The relative currents at -0.6 V were plotted against deposition time. A good straight line was obtained whose slope was $3.83 \times 10^{-3} \text{ s}^{-1}$ (Figure 6).

It was well within the range of both calibration curves in Figure 4. The concentration of unknown surfactant in the sample corresponds to 0.0759 mg L^{-1} TX-100 or 17.66 mg L^{-1} humic acid.

In Table 1 are presented data for surface-active substances of three freshwater systems as determined by the described electrochemical method. For comparison, the concentrations of dissolved organic carbon for the same samples are given too. As shown, the concentrations of organic matter are relatively high, 4.91 and 4.21 mg C/L for river water samples and 10.13 mg C/L for the wetland sample.

Neither of the calibration substances used, TritonX-100 or humic acid, can completely describe the composition and behaviour of naturally occurring organic surface-active substances in the investigated samples. It is important to mention that K_3 values in the (8), which are linearly proportional to the concentration of surfactant, at the same time depend on the characteristics of the adsorbed surface-active substances, both the naturally occurring and the calibration substances. Those characteristics are the diffusion coefficients, as well as the adsorption parameters, Γ_m and the differential capacities, which are included in the constant K_1 .

The relative standard deviation obtained for multiple analyses of the same solution containing surfactant such that TX-100 at the level $100 \mu\text{g L}^{-1}$ was 5%, which is fairly good. When concentrations of the mixture of the unknown surfactants from natural waters are measured, the choice of the calibration substance is relevant as mentioned in our previous papers [5, 24].

The advantage of TritonX-100 is that because it is widely used as standard, it allows comparison of different natural water samples. For example, the concentrations of surface-active substances, expressed in equivalent of TritonX-100, for samples in Table 1 are relatively low, as compared with other freshwater systems as determined by a.c. voltammetry [12, 13, 25] in spite of the fact that the concentrations of dissolved organic matter, in particular freshwater samples are high (Table 1).

If we compare the shape of the a.c. voltammetric curves of natural freshwater samples with those of model substances, it becomes clear that natural samples fit better to the humic-type substances. Taking into account the elemental composition of humic substances (corresponding to about 50% of organic carbon), it comes out that the concentration of surface-active substances of natural freshwater samples, when expressed in equivalents of humic substance, reveal quite well the chemical nature and behaviour of naturally occurring organic matter in the investigated samples. These are in accordance with our previous investigation of freshwater systems [12].

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