

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
3 (1997)

**SOME NEW TREATMENTS TO THE
ELECTROANALYSIS OF SURFACTANTS
(ELECTROCAPILLARY MEASUREMENTS,
ADSORPTION AND COMPRESSION
VOLTAMMETRY)**

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Received November 12, 1997

In this paper the principles of a few recent contributions to a further development of polarography and voltammetry are summarized. Special electrocapillary drop-time measurements, voltammetry of surfactants on renewed miniaturized stationary mercury electrodes, principles of the contractive and contractive & expansive measuring systems and three contributions to the theory of adsorption processes (adsorption isotherms, the peak potential shifts with concentration and the relative adsorptivity of surfactants) are discussed.

Special Electrocapillary Drop-Time Measurements

One of the experimental arrangements badly missed in laboratory practice is an instrument for exact studies of adsorption. That can be achieved through precise electrocapillary measurements of surface or interfacial tension of mercury as a function of experimental parameters like concentration of surface active

substances (SAS), type of solvent, electrode potential, temperature, etc. The electrocapillary apparatus described in the past [1] are today insufficiently sensitive towards traces of medium or strongly adsorptive SAS (usually ecologically or biologically important), the manipulation with them is cumbersome and highly demanding on the qualification of the measuring personnel, and hence they are unattractive.

At present the measurements are carried out [2] basically according to the original electrocapillary drop-time setting, with a special capillary using the regime of controlled convection, special accessories, etc. It is possible to work either with high precision, under strict experimental precautions eliminating vibrations, ensuring best geometric arrangement of the cell and drop-time detection at constant temperature which provided drop-time values (proportional to interfacial tension) of the order of 100 s with the precision reaching ± 0.002 s, or in an experimentally simpler less sophisticated way yielding drop-time values of reproducibility by an order of magnitude lower, yet still well acceptable.

In Table I are given results of an n -times repeated drop-time (t) measurement in 0.1 M H_2SO_4 at potential $E = -500$ mV vs. saturated calomel electrode (SCE); spindle-type capillary, upper inner diameter 50 μm , diameter of orifice 155 μm , rate of flow of mercury $m = 0.35$ mg s^{-1} .

High reproducibility of electrocapillary measurements is the essential condition for a successful study of the adsorption of SAS.

Table I Reproducibility of drop-time in 0.1 M H_2SO_4 at $E = -500 \pm 1$ mV (SCE), n is the ordinal number of measurement

n	1	2	3	4	5	6
t, s	59.98	59.98	59.97	59.98	59.98	59.98
n	7	8	9	10	11	
t, s	59.98	59.97	59.98	59.98	59.98	

Voltammetry of Surfactants on Renewed Miniaturized Stationary Mercury Electrodes

Various versions of the renewed miniaturized growing or stationary mercury drop electrodes have been described recently [2]. Usually they are of the pen type based on a mercury meniscus or a mercury droplet as the key components of the electrode systems.

The renewed miniaturized mercury electrodes used were divided according to terminology into three groups of the so-called micro-, semimicro- and minielectrodes (μE , $\text{s}\mu\text{E}$, mE), according to the electrode radius $r < 40 - 50$ μm for μE , $40 - 50$ $\mu\text{m} < r < 110$ μm for $\text{s}\mu\text{E}$, or 110 $\mu\text{m} < r < 160$ μm for

mE, resp.

The practical applicability of the miniaturized mercury electrodes is documented in Fig. 1 by voltammograms of the desorption peak of monensin in 0.1 M NaCl by the Adsorptive stripping tensammetry (AdST) method.

The increase of the prewave is due to an approximately as much as four-fold acceleration of the current determining processes due to diminution of the electrode.

The high mechanical stability of the miniaturized mercury drop and meniscus electrodes (unaffected by vibrations), the miniaturization of the entire set-up and the natural acceleration of transport of active solution components to the surface of these electrodes make them applicable for voltammetric measurements under the effect of ultrasound (tested at frequency of 36 and 42 kHz) in the usual solution volumes as well as in microvolumes and in capillary systems [3].

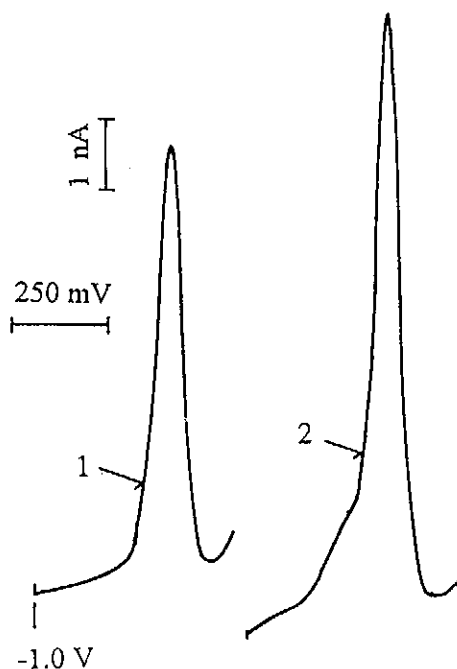


Fig. 1 Differential pulse voltammetry of 10^{-6} M monensin in 0.1 M NaCl; 20 mV s^{-1} , ampl. 50 mV ; potentials vs. Ag/AgCl electrode (1 M NaCl); curves 1, 2 - renewed stationary mercury drop semimicroelectrode $\text{MDs}_{\mu\text{E}}$, $r = 100 \text{ }\mu\text{m}$; t_{ac} : 1 - 50 s, 2 - 60 s

Principles and Basic Settings of the Contractive and Contractive & Expansive Measuring Systems

The contractive and contractive & expansive settings were applied for preparing renewed contracting mercury electrodes. The mercury drop electrodes prepared by the usual mechanism of drop growth, were contracted in a controlled manner, to be then, if desired, again expanded. The polarographic or voltammetric signals were recorded either in course of the contraction, after it at a stationary period, or during the following expansion phase.

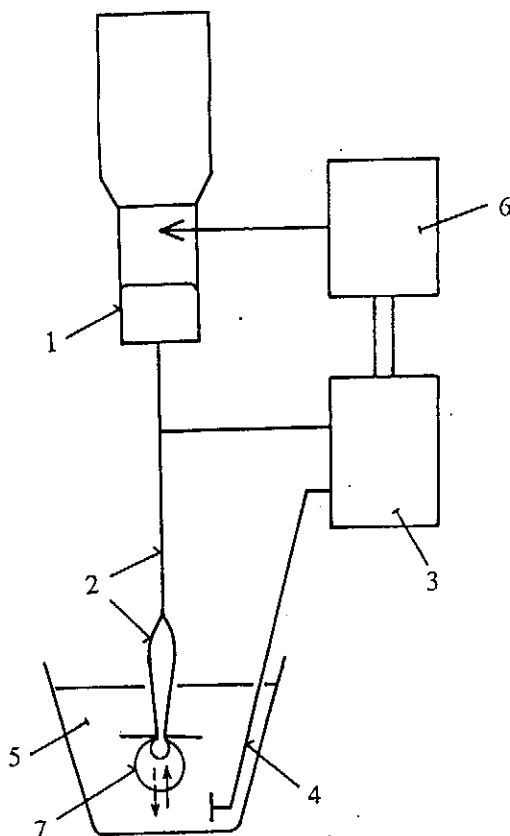


Fig. 2 A block scheme of a contractile RME (description in the text)

One version of the arrangement shown in Fig. 2 representing an example of the block scheme of a contractile (contractible, compressible) renewed mercury electrode (RME). The electrode with the spindle capillary 2 in the circuit of the measuring system 3 dips with the order electrode 4 into the solution 5. The measuring system is connected to the source of overpressure or vacuum 6 which controls the electrode 1. According to the pressure program a

mercury drop of usual size is first formed at the end of the capillary, which then gets contracted to the required extent during the suction phase. After the measurement the drop is renewed and the sequence of operations can be periodically repeated.

One example of utilization of the drop contraction is the effect of local accumulation of SAS due to the contraction. With 4×10^{-7} M monensin in 0.1 M KCl there is a difference if the differential pulse AdST curve is recorded with mercury drop grown to the final size ($r \approx 100 \mu\text{m}$) in the natural way or with a drop of the same final size but formed by contraction from the initial size of $r \approx 260 \mu\text{m}$. The latter way produces a much higher current signal.

Another case can be represented by the study of drop contraction utilizing a repeated cyclic voltammetry registration of $I - t$ curves, etc., starting, e.g., at the beginning of the contracting as well as the growing period; the curves indicate a strong effect of compression of the adsorbed layer during the mentioned contraction period.

Contributions to the Theory of Adsorption Processes

Brief Survey of Model, Semiempirical and Correlation Relations, Adsorption Isotherms

Examples of the relations [2] useful, e.g., for fitting adsorption isotherms, electrosorption, voltammetric or potentiometric dependences [5] can be expressed as follows

$$f_1(\theta) \exp f_2(\theta) = c \quad (1)$$

$$\frac{\theta}{1 - \theta} \exp \sum_{i=0}^n A_i \theta^i = c \quad (2)$$

or in other form

$$\frac{Y}{1 - Y} \exp \sum_{i=0}^n A_i Y^i = c - c_0 \quad (3)$$

where

$$Y = \frac{I - I_0}{I_m - I_0} \quad (4)$$

where the parameters $I - c$ represent, in a more general concept, a dependent and an independent variable, I_0 , I_m , A_i and n are parameters, and the pair

(c_0, I_0) are the coordinates of the origin of the coordinate system c ; I , θ is the surface coverage; $f_1(\theta)$, $f_2(\theta)$ are mathematical functions of θ .

I - c Tensammetric Dependences at low Concentrations

Further at low concentrations $I - c$ tensammetric dependences follow

$$I \sim K_1 \beta c - K_2 (\beta c)^2 \quad (4)$$

or

$$\frac{I}{c} \sim K_1 \beta - k_2 \beta^2 c \quad (5)$$

with the general constants K_1 and K_2 and the adsorption coefficient β .

The Peak Potential Shift E_p vs. c Dependence

For the dependence of potential shift E_p of an AdST peak on concentration c of a neutral molecule of SAS we may derive

$$\Delta E_p^2 = K_1 \ln c + K \quad (6)$$

Comparison of Interfacial Activity of Surfactants

On basis of voltammetric currents I in AdST the adsorptivity of selected SAS can be compared at low concentrations according to the formula

$$\left(\frac{I}{I_{ref}} \right)_c = \left(\frac{\beta'}{\beta'_{ref}} \right) \quad (7)$$

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