TENSAMMETRY IN COMBINATION WITH ADSORPTIVE ACCUMULATION OF SURFACE ACTIVE COMPOUNDS ON THE ELECTRODE SURFACE

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Recent substantial improvements in polarographic stripping analysis have resulted from the automation of the whole procedure where all necessary operations are programmed and the strictly reproducible conditions led to higher precision and accuracy. This gain has been assisted by the development of new types of sensors — mainly the static mercury drop electrode (SMDE). This electrode serves either as a hanging Hg electrode or as a dropping one. It can be used also as a dropping electrode "with constant surface area" after the drop is formed. The polarization of the dropping electrode in the moment when the surface area is just constant contributes to the decrease of charging current and the achievement higher sensitivity. At this static mercury drop electrode a needle valve is opening and closing the mercury flow through the capillary. Thus the drop is stopped at a determined instant of its growth. The movement of the needle is controlled from the polarograph. Using the SMDE as a dropping electrode a tapper dislodges the old mercury drop periodically from the capillary. The end of this glass capillary has a spindle shaped inner space [1]. The spindle shaped capillary yields drop-times of high reproducibility. In history there were many attempts to develop such a type of electrode. One of them was described by Gokhshtein et al. [2], and produced by the Academy of Sciences of the USSR. New types, where the drop formation and its size are controlled electronically are now on the market (PARC USA [3], Tesla Laboratorнí prístroje, CSSR).

A static mercury drop electrode (in combination with the automated polarograph PA3 produced by Tesla Laboratorнí prístroje Prague) was used by the present author for the further investigation of adsorptive phenomena. This work was started many years ago in connection with the study of the behavior of surface-active compounds by

means of oscillographic polarography with alternating current. [4]

Studying the oscillographic behavior of benzophenone and related compounds[5] it was observed that the incision on the \( \frac{dE}{dt} = f(E) \) curve becomes deeper if the electrode is first held for some brief time at a constant potential where adsorption of the compound takes place (Figure 1). Similar effects were also observed with some metal ions in solutions containing complex forming compounds or ions adsorbable at the electrode surface. The adsorptive accumulation effect was later used by many authors for the determination of various compounds; with different polarographic techniques being used as the stripping step. A survey is given in reference 6.

The aim of the present work is the study of the adsorptive accumulation of surface active compounds on the electrode surface in polarographic stripping analysis, where, during the stripping process, the desorption peak is recorded using differential pulse polarography (DPP).

RESULTS AND DISCUSSION

For adsorptive accumulation in stripping polarography there are suitable compounds yielding well-developed tensammetric DPP peaks in the concentration range from \( 10^{-5} \) M to \( 10^{-6} \) M at the dropping Hg electrode. Such strongly adsorbable compounds usually have an adsorption coefficient of about \( 10^{-5} \) M\(^{-1}\) or higher in the respective supporting electrolyte. The adsorption can be influenced by proper choice of supporting electrolyte or variations in its concentration as in the

Fig. 1. \( \frac{dE}{dt} = f(E) \) curve of benzophenone at polarization with single cycles of a.c. current. \( 4.10^{-5} \) M benzophenone in 1M H\(_2\)SO\(_4\) (at the first cycle the curve with the biggest indentation was obtained).