
**STABLE LAYERS OF OXYETHYLATED ALCOHOLS ADSORBED
ON THE SURFACE OF A HANGING MERCURY DROP
ELECTRODE UNDER TENSAMMETRIC CONDITIONS**

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The stability of adsorbed layers on a hanging mercury drop electrode was examined for oxyethylated alcohols (18-14, 18-10, 18-6, 10-14 and 6-14 where the first number denotes the number of carbon atoms in the n-alkyl chain and the second, the number of oxyethylene sub-units), Triton X-100 and for 18-14/10-14 and 18-14/Triton X-100 mixtures. The film stability was assessed in terms of the number of repetitions of the tensammetric peak recorded at the mercury drop after 5 or 10 min of adsorptive preconcentration. The most stable film is formed by the polyoxyethyleneoctadecyl monoethers, both alone and in the mixtures studied. The films are broken down by vigorous stirring of the solution for a certain time applying an electrode potential above the adsorption range of the surfactants.

Subjected to tensammetric study with accumulation, oxyethylated alcohols were found to form stable layers on the surface of a hanging mercury drop electrode (HMDE) (refs^{1,2}). The tensammetric peaks of sodium dodecylbenzene (Deterlon), polyoxyethyleneoctadecyl monoether (18-12 where the first number is the number of carbon atoms in the n-alkyl chain and the second is the number of oxyethylene sub-units) and their mixtures could be repeatedly recorded after a single preconcentration³. Similar experiments were performed in order to distinguish in AdST between "pure" tensammetric and faradaic processes⁴. Various voltammetric techniques have been employed to investigate the behaviour of stable phospholipid monolayers at mercury electrodes⁵⁻⁸. Stable films of Triton X-100 caused errors in trace element speciation by anodic stripping voltammetry with medium replacement⁹. The formation of such surfactant can bring about serious difficulties in the determination of trace concentrations of surfactants by tensammetry with accumulation at HMDE (ref.³).

Oxyethylated alcohols constitute the major group of nonionic surfactants used in Poland. If a surfactant includes more than 10 oxyethylated groups, its biodegrada-

tion is difficult. That is why oxyethylated alcohols, like some other surfactants, are natural water pollutants.

The purpose of the present work was to examine the stability of layers of various oxyethylated alcohols, Triton X-100 and their mixtures at HMDE based on repetition of the tensammetric peak at the same drop after a single preconcentration. The conditions of breakdown of the adsorbed film were also examined.

EXPERIMENTAL

A Radelkis OH-105 polarograph was used. The voltage scan rate was 400 mV min^{-1} , the alternating voltage amplitude was 2 mV. The apparatus was supplemented with a controlled-temperature HMDE equipment (Radiometer) fitted with an additional auxiliary molybdenum rod electrode. A saturated calomel electrode served as the reference. A small teflon beaker was placed in the glass cell so that the solution measured came in contact with teflon only. The potential was measured with an N-517 digital voltmeter (Mera-Tronic, Poland).

Triton X-100 was a commercial chemical (Merck), oxyethylated alcohols were synthesized at the Institute of Chemical Technology and Engineering, Technical University of Poznań.

Sodium sulfate used for the preparation of the base electrolyte was purified by double recrystallization and heating at 600°C . All solutions were prepared in water triply distilled from quartz. Freshly distilled water was invariably used. All vessels were glass and quartz. Aqueous $0.5\text{M-Na}_2\text{SO}_4$ served as the supporting electrolyte.

The solutions investigated were thermostatted at 25°C in the measuring flasks and then placed in the thermostatted (25°C) measuring cell and deaerated by nitrogen purging. Immediately before preconcentration, the stirrer was activated, the required preconcentration potential was adjusted and a fresh mercury drop was developed. The preconcentration time, which was 5 or 10 min, was measured from this moment. The tensammetric curve was recorded in the negative direction after a 10 s quiescent period. The recording of the curve was repeated immediately, starting from a potential near the peak beginning; the recording was only terminated after the peak vanished.

RESULTS AND DISCUSSION

The stability of the film adsorbed on the HMDE was investigated for the following oxyethylated alcohols: 18-14, 18-10, 18-6, 10-14 and 6-14, for Triton X-100 and for two mixtures, viz. 18-14/10-14 and 18-14/Triton X-100. The preconcentration potential was chosen based on our earlier study^{1,2}.

The adsorbed films of both the 18-14 and 18-10 surfactants were rather stable. Using a concentration of $50 \mu\text{g l}^{-1}$, preconcentration period of 5 min and a potential of -1.6 V , the tensammetric peaks could be recorded repeatedly at least 20 times. The peak heights decreased gradually; their dependences on the repetition cycle, which were obtained in a reproducible manner, are shown in Fig. 1 (curves *a* and *b*).

The curves in Fig. 1 differ in shape. For instance, for the peak of the substance 18-14 it took only four repetitions to drop to one-half of its starting value (after the preconcentration), whereas for the peak of the substance 18-10 to drop to one-half, eleven repetitions were necessary.

Because of the smaller peak height in the case of the third oxyethylated octadecanol, 18-6, a concentration of $100 \mu\text{g l}^{-1}$ and preconcentration periods of 5 and 10 min were applied. The results are shown in Fig. 1, curves *c* and *d*. When the longer preconcentration period was used, a relatively stable film was obtained for this substance as well.

The tensammetric curves of the substance 18-14 repeatedly recorded at a single mercury drop after a single preconcentration are shown in Fig. 2; the curves for the other two surfactants are similar.

Less stable films were obtained with the more hydrophilic oxyethylated alcohols with shorter n-alkyl chains, 10-14 and 6-14. Figure 3 demonstrates that the peak heights decrease rather rapidly so that the fifth peaks are very small in height. The peaks of the two substances are very broad. The tensammetric curves are shown in Fig. 4.

In the case of mixture of the surfactants 18-14 and 10-14, the stability of the film was also higher for the former compound. The concentration was $100 \mu\text{g l}^{-1}$ for each component, the preconcentration potential was -1.0 V and the preconcentration period was 5 min. In these conditions, as reported previously², the tensammetric peak of the substance 10-14 (the less negative peak in Fig. 5) is slightly higher than the corresponding peak of this surfactant alone. The other peak of the mixture (Fig. 5) is smaller in height than the peak of the substance 18-14 alone at the same concentration. This substance in the mixture gives rise to the more stable film although its peak height is lower. Really, this peak appears on multiple recording while that of the substance 10-14 is residual as early as the fifth repetition. The peak of the substance 18-14 decreased to one-half of its initial height on four repetitions, as in the case of this substance alone.

The effect of Triton X-100 on the peaks of oxyethylated alcohols^{10,11} suggests that the former substance also affects the film stability of the alcohols. Present in a concentration of $40 \mu\text{g l}^{-1}$, Triton X-100 brought about increase in the film

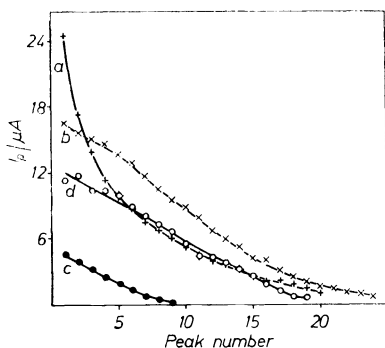


FIG. 1

Changes in the heights of tensammetric peaks recorded at a single mercury drop electrode after an adsorptive accumulation period for substances 18-14 (*a*), 18-10 (*b*), 18-6 (*c*, *d*) at concentrations ($\mu\text{g l}^{-1}$): *a*, *b* 50, *c*, *d* 100; preconcentration time (min): *a*-*c* 5, *d* 10; preconcentration potential -1.6 V

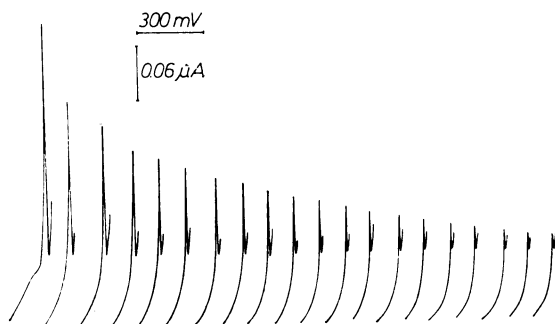


FIG. 2

Tensammetric curves of substance 18-14 recorded at a single mercury drop electrode after preconcentration period of 5 min, preconcentration potential -1.6 V; concentration of substance $50 \mu\text{g l}^{-1}$

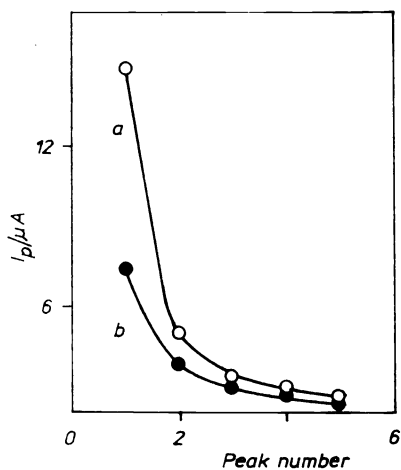


FIG. 3

Changes in the heights of tensammetric peaks recorded at a single mercury drop electrode after an adsorptive accumulation period of 5 min, preconcentration potential -1.4 V, for substances 10-14 (a) and 6-14 (b), present in a concentration of $100 \mu\text{g l}^{-1}$

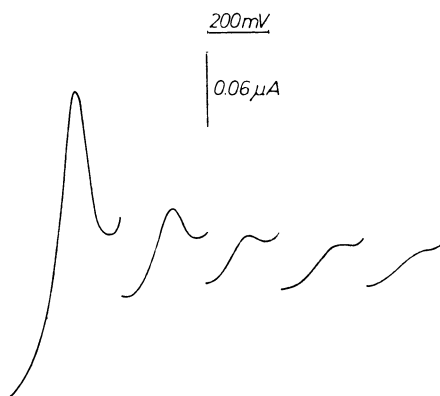


FIG. 4

Tensammetric curves of substance 10-14 recorded at a single mercury drop electrode after a preconcentration period of 5 min, preconcentration potential -1.4 V; substance concentration $100 \mu\text{g l}^{-1}$

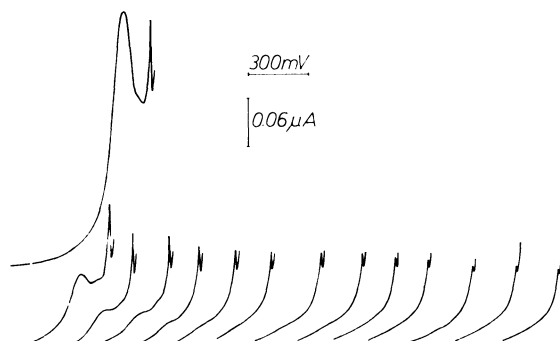


FIG. 5

Tensammetric curves of a 1 : 1 mixture of substances 18—14 and 10—14 recorded at a single mercury drop electrode after a preconcentration period of 5 min; total concentration $200 \mu\text{g l}^{-1}$

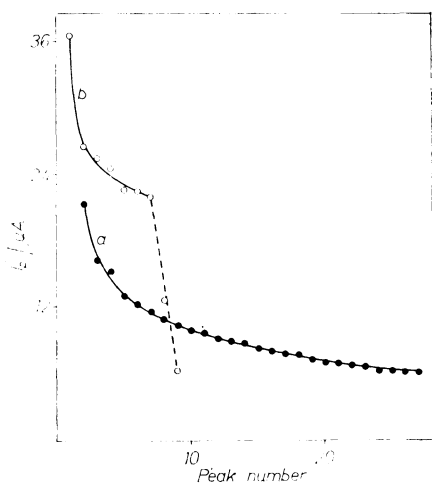


FIG. 6

Effect of Triton X-100 on the height of tensammetric peaks of substance 18—14 recorded at a single mercury drop electrode after an accumulation period. Concentrations ($\mu\text{g l}^{-1}$): 18—14 50, Triton X-100 40 (*a*), 1 000 (*b*). Before recording the 8th and 9th peaks, the electrode was kept for a minute in a stirred solution at a potential of -1.825 V

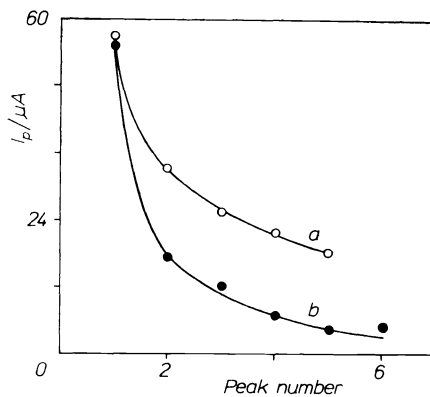


FIG. 7

Changes in the heights of tensammetric peaks of Triton X-100 recorded at a single mercury drop electrode after an adsorptive accumulation period of 5 min; preconcentration potential (V): *a* -1.0 , *b* -1.4 . Concentration of Triton X-100 $1\,000 \mu\text{g l}^{-1}$

stability of the substance 18–14 ($50 \mu\text{g l}^{-1}$); the peak height, however, increased to a small extent only. The results are shown in Fig. 6, curve *a*. The peak decreased to one-half of its initial value only in the seventh repetition, whereas if Triton X-100 was absent, this drop was recorded as early as the fourth repetition. Even during 25 repeated strippings the peak height decreased no more than about 70% with respect to its initial value after preconcentration. The preconcentration potential was -1.6 V in this case; this is the desorption potential of Triton X-100. The adsorbed layer did not break down on transferring the electrode after the preconcentration into a surfactant-free supporting electrolyte.

In the presence of Triton X-100 in a concentration of $1\,000 \mu\text{g l}^{-1}$, at which the growth of the tensammetric peak is appreciable, the film appears to be more stable. The peak height did not drop to zero even if the electrode was kept twice for a minute in a stirred solution applying a potential of -1.825 V , which is more negative than the desorption potentials of the two surfactants (Fig. 6). Total breakdown of the adsorbed layer took place on extending the stirring time to 3 min.

The stability of the adsorbed layer of Triton X-100 was investigated at a concentration of $1\,000 \mu\text{g l}^{-1}$, at which the effect on the peak heights of the oxyethylated octadecanols was stabilized^{10,11}; the preconcentration potential was -1.0 or -1.4 V . The results are shown in Fig. 7. Although the oxyethylated octadecanol was present in a concentration 20 times lower than Triton X-100, its adsorbed film was more stable than that of the latter. However, the film adsorbed at the preconcentration potential of -1.0 V was more stable than in the case of the preconcentration potential of -1.4 V . The tensammetric curves of Triton X-100 (5 min preconcentration at -1.4 V) are shown in Fig. 8.

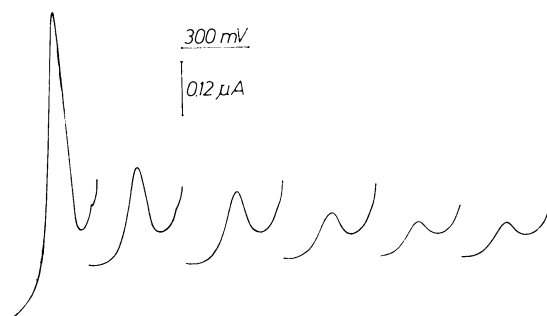


FIG. 8

Tensammetric curves of Triton X-100 recorded at a single mercury drop electrode after a preconcentration period of 5 min, preconcentration potential -1.4 V . Concentration of Triton X-100 $1\,000 \mu\text{g l}^{-1}$

The stable film of Triton X-100 was a source of error in trace element speciation by anodic stripping voltammetry with medium replacement⁹. This work gives evidence that the film can be completely broken down by vigorous stirring of the solution for a sufficient time, applying an electrode potential above the adsorption region of the surfactants. This procedure, in conjunction with the medium replacement approach, can be useful for removing surfactants as required in analytical practice.

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