

**INVESTIGATION OF ADSORPTION WAVES (V)  
THE OSCILLOPOLAROGRAPHIC BEHAVIOUR  
OF CERTAIN ANTHRAQUINONE MONO- AND DISULPHONIC ACIDS**

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Bylo zkoumáno chování některých antrachinonsulfonových kyselin a sledován vliv adsorptivních látek na zářezy elektrolytického a kapacitního původu.

With the classical polarographic method, on the ground of the effect of temperature, outflow velocity of mercury and concentration of depolarizer, the second wave on the cathodic reduction curve containing two waves of anthraquinone-1-sulphonic acid, anthraquinone-2-sulphonic acid, anthraquinone-1,5-disulphonic acid and anthraquinone-1,8-disulphonic acid had been found to be an adsorption post-wave on the first [1-4]. The limiting value of the height of these adsorption post-waves had reached at higher concentrations as those of the adsorption waves which had been studied in the fundamental investigations of R. Brdička [5-7]. Such type of adsorption waves after R. Brdička's investigations in several cases had been found [8-13] and the effect had been attributed to the slow formation of the adsorption layer [14]. When the compounds had been chemically reduced and the leucoforms had been polarographically oxidised [15] the first wave appeared with the same height and potential as in the cathodic reduction but the second one completely disappeared. This observation is in contradiction with others in which the adsorption wave after chemical reduction had been found with the same potential and height at the anodic side as at the cathodic, for example in case of Rosulidin GG [16]. It was impossible to explain this phenomenon on the ground of present theory of adsorption waves. However the results obtained by classical method show the second wave of the cathodic to be controlled by adsorption it seemed to be necessary to search after further proof of the role of adsorption in the reduction of anthraquinone mono- and disulphonic acids at the dropping mercury electrode.

As it is known at the oscillopolarographic  $dE/dt = f_1(E)$  curves the redox incisions of compounds, giving adsorption waves in classical polarography are accompanied with capacitive ones as it may be found in the case of quinin [17], lactoflavine [18] and desoxycorticosterone [21]. Therefore the  $dE/dt = -f_1(E)$  curves of the anthraquinone sulphonic acids were studied and the effect of other substances which are adsorbed at the dropping mercury electrode on the shape of the curves of these compounds was examined.

## Experimental Part

### Methodics

A „Very Low Frequency Oscilloscope“ Type 1538 (Orion EMG) had been used for the measurements with an adapter mainly of the same structure as it is described by J. Heyrovský and R. Kalvoda [20]. Several times recrystallized and distilled reagents have been used. 1 M-KOH solution served as supporting electrolyte. The potential of the dropping mercury electrode refers to a silver wire electrode.

## Results and Discussion

At the cathodic side of the  $dE/dt = f_1(E)$  curve of all the four compounds two incisions are observable (Fig. 1a—d). At anthraquinone-1-sulphonic acid the depth of the incisions is nearly equal, at anthraquinone-2-sulphonic acid the second is deeper.

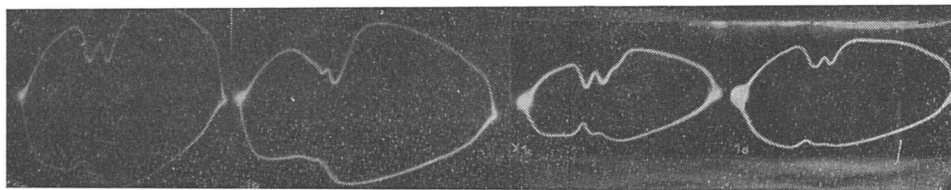


Fig. 1.  $dE/dt = f_1(E)$  curves of the anthraquinone sulphonic acids in 1 M-KOH. Concentration of the acid  $2 \cdot 10^{-4}$  M: a) anthraquinone-1-sulphonic acid; b) anthraquinone-2-sulphonic acid; c) anthraquinone-1,5-disulphonic acid; d) anthraquinone-1,8-disulphonic acid.

With the variation of concentration of depolarizer seems the first incision to be a redox one and the second in connexion with capacitive effects. These results are not in contradiction with those of H. Berg [19], who found only one incut at the mono-sulphonic acids because he used a supporting electrolyte containing 50 % ethanol, and this solvent in rather smaller amounts deform the curves (Fig. 2).

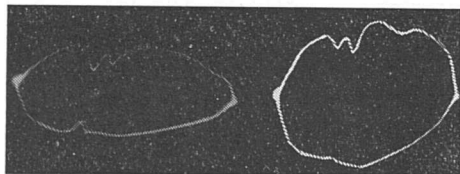


Fig. 2. The effect of ethanol (10 %) on the  $dE/dt = f_1(E)$  curve of  $1 \cdot 10^{-4}$  M anthraquinone-1-sulphonic acid; 1 M-KOH.

Fig. 3.  $dE/dt = f_1(E)$  curve of  $1 \cdot 10^{-4}$  M anthraquinone-1-sulphonic acid after addition of  $1 \cdot 10^{-4}$  M Indigosolgelb V; 1 M-KOH.

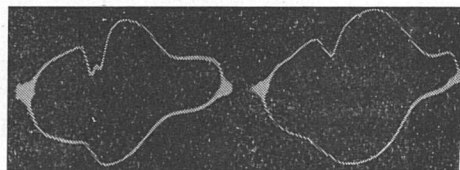


Fig. 4. The effect of dimethylformamide on the  $dE/dt = f_1(E)$  curve of  $2 \cdot 10^{-4}$  M anthraquinone-1,8-disulphonic acid; 1 M-KOH. Concentration of dimethylformamide: a) 3 %; b) 20 %.

The effect of Indigosolgelb V [22] causes some deformation at the shape of the incuts but it seems to be adsorbed with nearly the similar strength at the surface of mercury as the anthraquinone sulphonic acids (Fig. 3).

The addition of N,N'-dimethylformamide to the solution of the sulphonic acids first only causes some deformation (Fig. 4a) but at higher concentration eliminates the second incut (Fig. 4b) as it behaves with the second wave of the  $i$  vs.  $E$  curves [23].

Dioxane even in small amounts eliminates the second incut corresponding to the classical polarographical results.

The effect of *n*-butanol is rather weak being adsorbed at more positive potentials as the incuts of the anthraquinone sulphonic acids appear (Fig. 5). In some cases it destroys even the first incision.

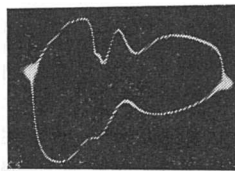


Fig. 5. The effect of buthanol (3 %) on the  $dE/dt = f_1(E)$  curve of  $2 \cdot 10^{-4}$  M anthraquinone-1,8-disulphonic acid; 1 M-KOH.

On the ground of these results the first incision of the anthraquinone sulphonic acids investigated may be regarded a more-less reversible redox one and the second to be controlled by the adsorption of depolarizer. This is proofed by the behave of the incisions and the effect of adsorbable substances on them: the second incision changes more sensitively with the appearance of surface active substances.

*The authors feel to their gelightful duty to aknowledge to Mr. T. Damokos, for his valuable help in the experimental work.*

### Summary

In addition to classical polarographical investigations concerning with the adsorption properties of 4 anthraquinone mono- and disulphonic acids the oscillopolarographic study of these compounds have been carried out.

## ИССЛЕДОВАНИЕ АДСОРБЦИОННЫХ ВОЛН (V) ОСЦИЛЛОПОЛЯРОГРАФИЧЕСКОЕ ПОВЕДЕНИЕ НЕКОТОРЫХ АНТРАХИНОНМОНО- И ДИСУЛЬФОНОВЫХ КИСЛОТ

Д. ПАЛЫИ, Ф. ПЕТЕР

Объединенные химические заводы в Будапеште

Исследовательский институт текстильной промышленности в Будапеште

Исследовалось поведение некоторых антрахинонсультфоновых кислот и влияние некоторых адсорбирующихся веществ на зубцы электролитического и емкостного тока.

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## Diskussionsbeiträge

H. Berg betont, dass es in neutralen Lösungen beim Potential der Abscheidung der alkalischen Metalle zur Alkalisierung der Elektrodenoberfläche kommt, was den anwesenden Depolarisator chemisch beeinflussen kann. Bei seinen eigenen Versuchen beobachtete er, dass es zur chemischen Reaktion zwischen den Amalgamen und den Anthrachinonen kommt.