

ADSORPTION PHENOMENA IN SOLUTIONS OF SOME ANTHRAQUINONESULFONIC ACIDS: FACTORS RESPONSIBLE FOR POSTWAVES

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The comparison of the adsorption of anthraquinone-1,5-disulfonic, anthraquinone-1-sulfonic acids and respective reduced compounds shows that the appearance of polarographic adsorption waves is connected with partial (in the case of postwave) and complete (in the case of prewave) inhibition of the reduction process by the reduction products. The number of electrons involved in the reaction has been determined ($n = 2$ and 4 for di- and monoacid, respectively). Using rotating disc electrode the order of the electrode reaction equal to one has been found.

Derivatives of anthraquinone, particularly sulfonic acids, exhibit a number of valuable properties, including adequate solubility for polarographic purposes in combination with good adsorbability on mercury. Hence, solutions of these compounds lend themselves to studies of the effect of adsorption upon electrochemical reduction of organic compounds.

Polarographic studies of anthraquinone derivatives were carried out earlier¹⁻⁴. Furman and Stone¹ detected postwaves on polarograms of some anthraquinone derivatives containing an NH_2 group, which, in their opinion, is indicative of stability of the semiquinones resulting from reduction of these compounds.

Further polarographic studies of anthraquinone-1-sulfonic acid² and anthraquinone-1,5-disulfonic acid³ also showed the existence of postwaves on the polarograms. In this case, the dependence of wave heights on concentration, temperature and mercury column height was examined. According to Peter and coworkers²⁻⁴ as the concentration of anthraquinone-1-sulfonic acid and anthraquinone-1,5-disulfonic acid increases, the main wave and the postwave become distinctly separated and the currents corresponding to both waves increase; however, at a concentration of $8 \cdot 10^{-4}$ mol/l the postwave current reaches its limiting value and does not vary any more. The effect of temperature was studied in the range of $+2$ to $+55^\circ\text{C}$. It has been established that the half-wave potential shifts toward more positive potentials and both waves practically merge. The plot of dependence of the postwave current on the height of mercury column essentially a straight line, just as it should be in the case of adsorption waves. However, polarograms at anthraquinonesulfonic acid concentrations less than 10^{-3} mol/l show a maximum whose origin is not discussed by the authors.

The fact, that the above mentioned sulfonic acids show a postwave under cathodic polarization of mercury is of interest as our attempts to find, in the literature, a reversible system showing

a true postwave, failed. The only exceptions might be phenoxyfranine⁵ and the reversible bis-diethylcarbamyl disulfide-diethyl carbamate system⁶.

Naturally, in redox systems showing prewaves under cathodic polarization of mercury, postwaves must invariably be observed in the case of anodic polarization. The present work deals primarily with postwaves occurring in the course of reduction of organic compounds at the dropping mercury electrode. But first let us discuss the possible causes of the appearance of adsorption postwaves.

According to Brdička⁵, the formation of adsorption postwaves can be explained as follows: let us assume that the energy of adsorption of the oxidized form is sufficiently great for the coverage of the electrode surface by this form to represent a value approaching unity at a sufficient departure from the equilibrium potential toward the cathodic values. Let us also assume that the presence of a reduced form in the solution does not decrease the adsorption of the oxidized form. When dealing with monolayer adsorption, the latter condition means that the energy of adsorption of the oxidized form is much greater than that of adsorption of the reduced form. However, in the case of polylayer adsorption, this condition is not absolutely necessary. At the same time, in accordance with the Nernst formula, a particular relation between the concentrations of the oxidized and reduced forms must be maintained near the electrode (it is assumed that the velocity of the change of the potential is so small that the above relation has time to be established at any potential).

Adsorption of the oxidized form at the electrode reduces its concentration near its surface, hence, sharply reduces the relation C_{ox}/C_r . In order to bring this relation to an equilibrium value, in accordance with the Nernst formula, the quantity of electricity to pass through the electrode must be $Q = nFT$.

If the electrode surface increases continuously in time (dropping mercury electrode), the following current will flow continuously through the electrode to compensate for the loss of the oxidized form near the electrode:

$$I = dQ/dt = nFT/(dS/dt) . \quad (1)$$

Thus, anodic current must flow continuously through the electrode even if a limiting cathodic diffusion current is observed in the system without predominant adsorption of the oxidized form. Consequently, after the wave ceases to rise (Fig. 1, curve 3, portion A), the current does not reach the value of the limiting diffusion current at once but forms a step on the curve (portion B). Over portion B the current is partially limited by the rate of the surface growth. Portion C exhibits all properties of diffusion current. The postwave proper is represented by the dashed line, however, it has become traditional in the literature to regard the step (dash-dot line) as the postwave, which has the same height as the preceding portion. According to this tradition portion C will be regarded here as the postwave and the difference in height between portions C and B will represent the value of the adsorption current.

Hence, the occurrence of a postwave in studies involving a dropping mercury electrode is attributed to the operation of a "pump" that sucks the oxidized form from the space surrounding the electrode. At a sufficient departure from the standard potential, adsorption of the oxidized form and, consequently, the anode current are decreased to such an extent that the polarogram is no more distorted — portion B reaches the value of the limiting diffusion current.

It should be emphasized, however, that for marked adsorption of the oxidized form to occur at potentials greatly differing from the standard redox potential of the system, the energy of adsorption of this substance must be high because the concentration of the oxidized form near the electrode is small under these conditions.

However, the occurrence of adsorption waves is also possible involving a mechanism which differs from that proposed by Brdička. Let us assume that the adsorption of the reaction product takes place on the electrode surface irreversibly, that is the substance forming as a result of an electrochemical reaction remains on the electrode surface. If it is further assumed that the electrochemical reaction is possible only on the surface free of the reaction product, the rate of the process as a whole will be determined by the rate of free surface formation. In this case the expression $nF\Gamma_r$ will serve as a measure of the amount of the transformed substance, while the quantity of the electricity passed through the electrode will be

$$Q = nF\Gamma_r S. \quad (2)$$

Then, the current is determined from the following expression:

$$dQ/dt = nF\Gamma_r (dS/dt). \quad (3)$$

Eq. (3) is identical with Eq. (1) derived by Brdička for adsorption waves in the

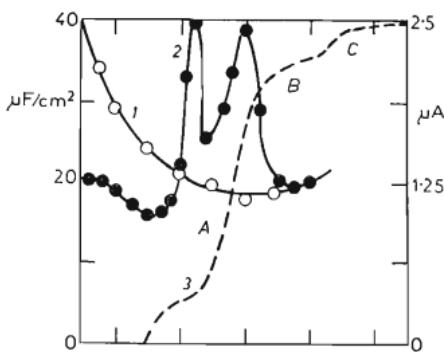


FIG. 1

Differential capacity (C) versus electrode potential in a solution of $5 \cdot 10^{-4}$ mol/l 1,5-disulfonic acid in 0.05M- Na_2SO_4 (2); 1 differential capacity of the supporting electrolyte; 3 polarographic curve

case of fully reversible systems. In the case under consideration, the polarogram will also show a prewave but it will result from the blocking of the surface by the reduced form.

When the potential shifts to the negative side, there inevitably comes a moment at which, due to various reasons (including desorption of the reaction product from the electrode surface or loosening of the adsorption layer whereby the electrochemical reaction on the occupied surface becomes possible), the process involves the entire electrode surface. In this case, the above-mentioned prewave due to hindering by the reaction products is followed on the polarogram by the main wave. As the temperature rises, the reaction product does not block the electrode surface any more, and the prewave disappears. Thus, prewaves in irreversible systems behave in many respects similarly to those in reversible systems although different mechanisms are responsible for their occurrence. As can be seen from Eq. (3) if the adsorption process is completely irreversible, the magnitude of the prewave current can be used in calculating the adsorption of the reaction products.

If the adsorption of the reaction product is particularly reversible, *i.e.* when only a part of the adsorbed substance remains on the electrode surface ($\Gamma_1 < \Gamma_r$), the "prewave" current increases sharply due to the blocking of the surface, and the lower the value of Γ_1 in comparison to Γ_r , the closer is the "prewave" situated to the limiting diffusion current. Under certain conditions the prewave may be so close that the limiting diffusion current appears as a step on the polarogram simulating a postwave.

Thus, in analyzing the reduction process one must always differentiate between true postwaves or prewaves according to Brdička and adsorption waves due to the blocking of the electrode surface. This is particularly important because in the latter case the polarographic behaviour of postwaves (dependence on the mercury column height, on temperature and on solution concentration) may be the same as in the case of postwaves according to Brdička. In this connection it becomes interesting to carefully study any adsorption waves that may in fact be true postwaves. Of particular interest in this respect are the adsorption phenomena observed during reduction of anthraquinone-1-sulfonic acid and anthraquinone-1,5-disulfonic acid and extensively investigated by Hungarian scientists²⁻⁴.

EXPERIMENTAL

The polarographic behavior of anthraquinonesulfonic acids was examined using an LP-7 polarograph (Laboratorní přístroje, ČSSR) with a standard three-electrode cell; the reference electrode was a saturated calomel electrode, the mercury pool served as the auxiliary electrode. The parameters of the capillary were as follows: drop time, $\tau = 2.9$ s; mercury flow rate, 2.84 mg/s. Purified argon was bubbled through the solution prior to and in the course of measurement. The differential capacity was measured in solutions of anthraquinone-sulfonic acids using a hanging-drop cell described in detail in an earlier work⁷. After each measurement a new drop was

formed. A platinum cylinder coated by mercury was used as the auxiliary electrode. The measurements were made using an ac bridge similar to the one described earlier. The operating frequency was 415 Hz. The calculations were carried out using a parallel-series circuit arrangement (Fig. 2).

The adsorption was determined chronopotentiometrically using a hanging-drop cell with a saturated calomel electrode used as the reference and the mercury pool used as the auxiliary electrode. The electrode was kept at a given potential for a time period sufficient for establishment of the adsorption equilibrium, then, without breaking the circuit, it was operated in the galvanostatic mode and a potential-*versus*-time curve was recorded (on a memory scope). The duration of the arrest depended on the polarizing current density in the galvanostatic mode and usually varied from 0.1 to 20 ms. For calculation of the true amount of the charge involved in reduction of the adsorption layer an extrapolation was made in the coordinates: $i\tau - 1/\sqrt{i}$ where i is the polarizing current density in A/cm^2 , τ is the transition time in s, and Q is the quantity of electricity, corresponding to the transition time.

The reagents were purified by double recrystallization from a bidistillate, and the solutions were also prepared using bidistilled water.

The kinetics of reduction of anthraquinone-1,5-disulfonic acid was studied using an amalgamated gold rotating disk electrode. The electrode surface was regenerated before each measurement (point-by-point) by suspending a mercury drop at the electrode with subsequent detachment of the drop while the electrode was rotating at a speed of 10 000 rpm. The measurement procedure and the cell for taking polarization curves with the aid of a rotating disk electrode have been described elsewhere⁷.

RESULTS AND DISCUSSION

Polarographic Study of Anthraquinonesulfonic Acids

The polarograms of solutions of anthraquinone-1,5-disulfonic and anthraquinone-1-sulfonic acids at concentrations ranging from 10^{-4} to 10^{-3} mol/l in 0.05M- Na_2SO_4 , reveal a clearly defined postwave ~ -0.9 V in the case of anthraquinone-1-sulfonic acid and -1.2 V in the case of anthraquinone-1,5-disulfonic acid. The height of this postwave increases with the concentration of the oxidized form more slowly than that of the main wave (Fig. 3). Thus, the waves under examination behave as true postwaves in all respects. However, when the concentration of the above anthraquinonesulfonic acids is lowered (below $5 \cdot 10^{-4}$ mol/l), a prewave appears on the polarograms of both anthraquinone-1,5-disulfonic and anthraquinone-1-sulfonic acid solutions (Fig. 1). The half-wave potential of the prewave is -0.45 V in the anthraquinone-1,5-disulfonic acid solution and -0.35 V in the anthraquinone-1-sulfo-

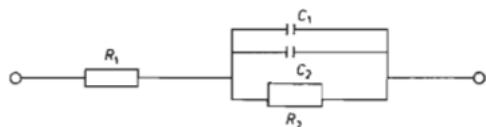


FIG. 2
Circuit used for calculations

nic acid solution. Hence, the difference between the half-wave potentials of the main wave and the prewave in the solutions of these compounds is 300 mV. Such a difference in half-wave potentials corresponds, according to Brdička's theory, to an unusually high value of the adsorption energy in the case of a two-electron process; hence, this prewave cannot be explained in terms of Brdička's theory, although prewaves undoubtedly have an adsorption nature, tending to a limit when the concentration of the reacting substance is increased. There is an other difference between the observed and the true prewaves. It is known that a true prewave tends to disappear when the temperature rises. However, in the case of the anthraquinonesulfonic acids under investigation, a rise in temperature leads only to an increase in the limiting current of the prewave (Fig. 4). This specific feature of the observed prewaves is an unambiguous indication that the observed prewaves are due to blocking of the electrode surface by a reaction product. Similar prewaves were observed by Zuman^{8,9} and Frumkin and coworkers¹⁰ in their studies of the reduction of tropylium ions.

The assumption of the electrode surface being blocked by the reaction product explains the features of the prewaves in solutions of anthraquinone-1-sulfonic and anthraquinone-1,5-disulfonic acids. However, polarographic studies cannot provide an unambiguous answer as far as the nature of the postwaves is concerned.

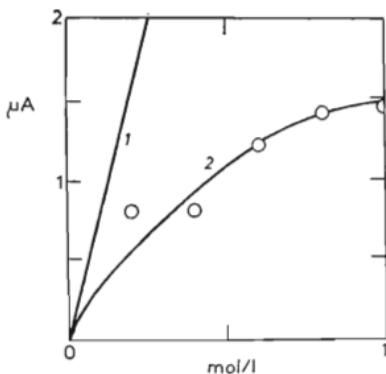


FIG. 3
Limiting diffusion current (portion C, Fig. 1) versus concentration 1; 2 postwave current versus concentration

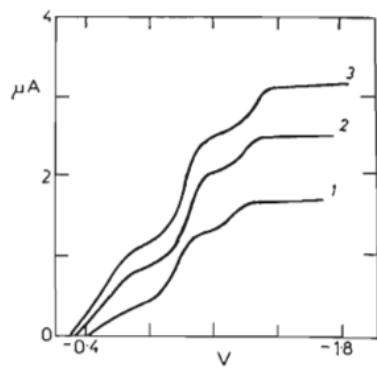


FIG. 4
Temperature dependence of the current versus electrode potential curve for 1,5-disulfonic acid. Temperature (°C): 1 18; 2 50; 3 80

*Analysis of Adsorption of Anthraquinone-1,5-disulfonic
and Anthraquinone-1-sulfonic Acids*

Fig. 1 represents typical curves showing the differential capacity of a mercury electrode *versus* potential in anthraquinonesulfonic acid solutions. These curves suggest that at potentials more positive than the beginning of the upward slope on the polarogram the capacity of the double layer is much lower than that in the supporting electrolyte alone which is a clear indication that these anthraquinonesulfonic acids are adsorbed on mercury in the above potential range. In addition, two maxima can be clearly seen on the $C-E$ curves. The potential of the left maximum approaches the half-wave potential of the main wave on the polarogram, which is indicative of the process being substantially reversible. From the $C-E$ curve it can be also seen that immediately after the left-hand maximum the curve drops abruptly in the solutions of both compounds and follows by the right-hand maximum after which the capacity in the solutions containing anthraquinone derivatives becomes equal to that for the supporting electrolyte. This means that at potentials approaching -1.2 V (corresponding to currents approaching the limiting diffusion current) the electrode surface is free of the adsorbed organic substance. Unfortunately, the application of the differential capacity measurements (just as all other methods with the exception of chronopotentiometry) cannot give an insight into the character of the adsorbed species. Chronopotentiometry enables both quantitative and qualitative analyses of the composition of the adsorption layer. The chronopotentiograms of the cathodic and anodic processes (Fig. 5) taken in solutions of anthraquinone-1-sulfonic acid (10^{-5} to 10^{-3} mol/l in $0.05M\text{-Na}_2\text{SO}_4$) show two arrests. The durations of both arrests

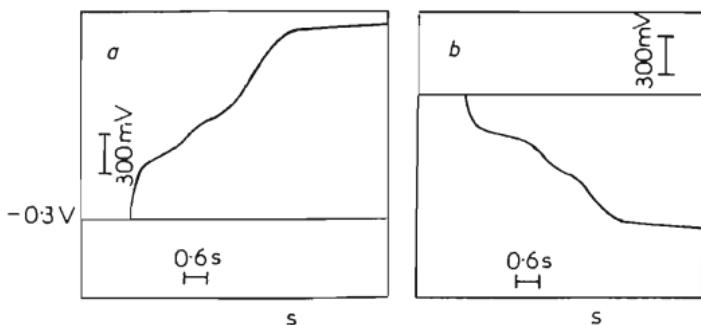


FIG. 5

Chronopotentiograms of the cathodic (a) and anodic (b) processes of anthraquinone-1-sulfonic acid

were used in determining the amount of adsorption of the oxidized (Γ_{ox}) and reduced (Γ_r) forms from the formula:

$$nF\Gamma = Q/S, \quad (4)$$

where Γ is the amount of adsorption (mol/cm^2), n is the number of electrons involved in the reaction, F is the Faraday constant, S is the electrode area (cm^2), and Q is the extrapolated value of the quantity of electricity passing through the electrode during the transition time.

Represented in Fig. 6 is the adsorption of the oxidized and reduced forms *versus* potential. Also shown for comparison is a polarogram taken under the same conditions.

Comparison of Fig. 6 with Fig. 1 and the polarogram indicates that, in accordance with the results of analysis of the capacity curve, the adsorption of the oxidized form (Γ_{ox}) of both sulfonic acids markedly increases in the proximity to the foot of the polarogram, where the reaction product appears. As the potential shifts further to the negative side, the value of Γ_{ox} drops reaching zero at the point where the postwave reaches its limiting current. The maximum value of Γ_{ox} is $1.3 \cdot 10^{-10} \text{ mol}/\text{cm}^2$ for anthraquinone-1,5-disulfonic acid, ($n = 2$) and $1.15 \cdot 10^{-10} \text{ mol}/\text{cm}^2$ for anthraquinone-1-sulfonic acid ($n = 4$). The adsorption of the reduced form (Γ_r) sharply increases as the potential shifts to the negative side, eventually reaching the value of $1.7 \cdot 10^{-10} \text{ mol}/\text{cm}^2$ at a potential corresponding to the prewave limiting current. Then, the value of Γ_r decreases in the solutions of both compounds and reaches zero at a potential corresponding to the limiting diffusion current. The resulting relationship between Γ_{ox} and Γ_r and potential for both compounds coincides with that observed in the case of other redox systems and reveals no irregularities. An important finding is that at the potentials of the left-hand peak on the differential

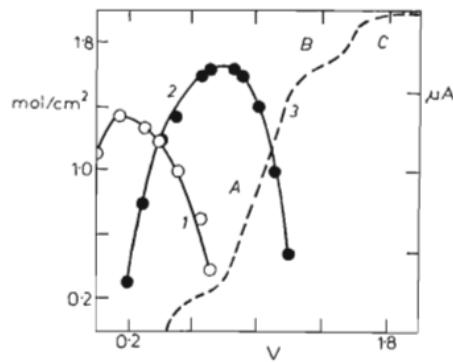


FIG. 6

Adsorption (Γ) *versus* electrode potential (E).
 1 Oxidised form; 2 reduced form of 1,5-di-sulfonic acid, $5 \cdot 10^{-4} \text{ mol/l}$, in $0.05\text{-Na}_2\text{SO}_4$; 3 polarogram, $n = 2$

capacity curves the electrode surface is covered by a considerable amount of the adsorbed substance, which means that this cannot be an adsorption – desorption peak. On the other hand, the right-hand maximum on this curve is definitely an adsorption – desorption peak since at potentials corresponding to this peak a sharp drop is observed on the adsorption–potential curve for the reduced form. Another interesting is that at potentials corresponding to the limiting current of the prewave the total adsorption is almost 1.5 times greater than the maximum adsorption of the oxidized form. However, at perceptible negative charges at the electrode, the adsorption of the reaction product decreases, that of the oxidized form drops to zero, and a steep upward slope is observed on the polarogram.

Thus, comparison of polarographic and chronopotentiometric data unambiguously shows that in the case of anthraquinone-sulfonic acids neither the prewave nor the postwave is an adsorption wave according to Brdička but is associated with complete (prewave) or partial (postwave) inhibition of the electrochemical process by the reaction products.

Study of the Kinetics of Electrochemical Reduction of Anthraquinone-1,5-disulfonic Acid

The measurements were taken in solutions of anthraquinone-1,5-disulfonic acid ($5 \cdot 10^{-4}$ mol/l) in 0.05M-Na₂SO₄. Polarography with a rotating disc electrode shows

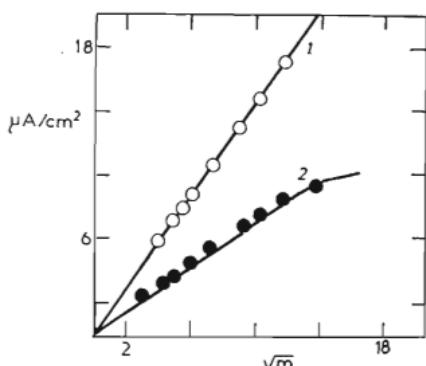


FIG. 7

Current density *versus* $(\sqrt{m} \text{ (min s}^{-1}) \cdot 5 \cdot 10^{-4} \text{ mol/l})$, 1,5-disulfonic acid in 0.05M-Na₂SO₄. 1 limiting diffusion current; 2 current at -0.42 V

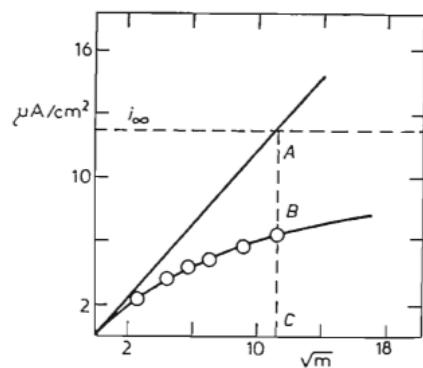


FIG. 8

Determination of the order of electrochemical reduction of 1,5-disulfonic acid

only one reduction wave, which is a proof that the prewave observed on polarograms taken with the use of a dropping mercury electrode is not due to impurities; as is known, adsorption waves tend to disappear when a rotating disc electrode is used.

Fig. 7 represents the dependence of the limiting diffusion current density (i_d) and the current density (i) corresponding to the potential of -0.42 V on the square root of the rotating speed of the electrode (m , rpm). As can be seen in Fig. 7 curve 2 departs from the straight line which is indicative of a complex kinetics of the process.

The order of the electrochemical reduction of the sulfonic acids under investigation was determined by a method proposed by Frumkin and Tedoradze¹¹ and found to equal unity for both compounds (Fig. 8).

It was shown¹² that anthraquinone derivatives can be reduced involving a total of two as well as four electrons. In this connection it was interesting to separately determine the number of electrons involved in the reaction and the diffusion coefficients for both anthraquinonesulfonic acids. These values were determined by a method proposed earlier¹³. The diffusion coefficient (D) and the number of electrons involved in the reaction (n) were found to be: (1) anthraquinone-1,5-disulfonic acid $D = 3.09 \cdot 10^{-6}$ cm 2 /s; $n = 2$; (2) anthraquinone-1-sulfonic acid $D = 3.25 \cdot 10^{-6}$ cm 2 /s; $n = 4$. These values agree well with those determined for other anthraquinone derivatives, such as 1,2-dihydroanthraquinone-3-sulfonic acid ($D = 3.45 \cdot 10^{-6}$ cm 2 /s).

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