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**INTERFACIAL INTERACTIONS BETWEEN AQUEOUS SOLUTIONS OF 4,4'-BIPYRIDYL AND MERCURY**

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From analysis of electrocapillary curves obtained by drop-time measurements with spindle-type capillary and the method of controlled convection the data on reversible equilibrium adsorption of 4,4'-bipyridyl on mercury from aqueous 0.1M solutions of Na<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> were obtained. In neutral solution 4,4'-bipyridyl is strongly adsorbed: at potential of maximum adsorption the Langmuir coefficient  $\beta = 1.4 \cdot 10^2 \text{ m}^3 \text{ mol}^{-1}$  and  $\Gamma_m = 1.8 \cdot 10^{-6} \text{ mol m}^{-2}$ ; in acid solution the adsorption of the doubly protonated 4,4'-bipyridylium cation is weaker and its potential dependence goes through a minimum. The increase of adsorption of the bipyridylium cation and a simultaneous increase of negative charge with increasing negative potential are explained by charge transfer in adsorbed state. The electroreduction of 4,4'-bipyridyl is preceded by formation at the electrode surface of a layer of sparingly soluble salt of the bipyridyl cation radical.

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4,4'-bipyridyl (BP) is the parent compound of the 1,1'-bisquaternary derivatives known also as the viologens<sup>1</sup> which have been recently finding increasing use in various fields (*cf.* references in<sup>2-4</sup>). The cause of the interest in these compounds lies in their two special properties: the first is their ability to accept electron in a fast reversible reaction forming a relatively stable cation radical of a characteristic blue colour, and the second is their ability to enter into weak interactions with various components of homogeneous and heterogeneous systems which is the cause of their specific adsorbability. Both these properties can be conveniently studied with the use of the dropping mercury electrode.

For estimation of the importance of the heterogeneous factor in photoreactions and in catalytic processes involving BP and its derivatives in water<sup>5,6</sup> we needed some reliable data on interaction of these compounds with simple defined surfaces; the adsorption of BP on mercury was the first choice for study. Adsorption was recognized as an important process in electroreduction of BP<sup>7</sup>; the differential capacity of mercury electrode in solutions of BP was measured<sup>8</sup> and a group of authors<sup>9,10</sup> studied the adsorption of BP on mercury using the method of capillary electrometer. We applied for the same purpose the new method of drop-time measurement with controlled convection<sup>11,12</sup> which allowed us to follow adsorption of BP from solutions of concentrations as low as  $10^{-6} \text{ mol l}^{-1}$ .

## EXPERIMENTAL

The studies of electrocapillarity were carried out by measuring the drop-time of a dropping mercury electrode (DME) with the use of a spindle-type capillary<sup>13</sup> (inner diameter of the upper part 50  $\mu\text{m}$  and of the orifice 155  $\mu\text{m}$ ). Depending on the height of the mercury reservoir the capillary yielded drop-times between 40 and 110 s. The method of controlled convection<sup>11</sup> was applied consisting in stirring the solution during the growth of the drop until about 10 s before its detachment. The drop-time corresponding to the attainment of adsorption equilibrium was checked by gradually prolonging the time of stirring of the solution. For polarographic studies spindle-type capillary of a short drop-time and Smoler's type capillary (bent at 90° and cut at 45°) were used. The polarograph PA 3 (Laboratorní přístroje, Prague) served as source of polarization voltage in a two-electrode cell for electrocapillary measurements with SCE as reference electrode separated from the measured solution by an electrolyte bridge filled with 0.5M Na<sub>2</sub>SO<sub>4</sub>. Potential of the DME was controlled by means of a digital voltmeter NR 50 (Metra, Blansko) with precision of  $\pm 1$  mV. The drop-time was measured with an electrical device described elsewhere<sup>14</sup>. For recording the polarographic curves the two-electrode type LP 60 polarograph (Laboratorní přístroje, Prague) was used with a cell with separated SCE as reference.

4,4'-bipyridyl of analytical purity grade was the product of Lachema, Czechoslovakia. All solutions were prepared from analytical purity grade chemicals and bidistilled water. Before measurements the solutions were deaerated by a stream of purified nitrogen; during measurements the nitrogen was passed above the solution. The work was carried out at constant room temperature of 20°C.

## RESULTS AND DISCUSSION

### Interactions in the Potential Region Beyond Electrode Reaction

#### *Polarographic Measurements*

First qualitative information about adsorbability of a substance on mercury can be obtained from d.c. polarographic curves recorded with high sensitivity. The electroreduction of BP begins in acid solutions at potentials below  $-0.6$  V and in neutral solutions below  $-1.0$  V (SCE), the exact values depending on concentrations of BP and on composition of the solution. This represents the negative limit of the potential range over which the interaction of BP with mercury in absence of an electrolytic process can be studied.

When BP is added into solutions of neutral electrolytes or into buffers of pH about 6 and higher, the charging current shows the classical picture of adsorption: in consequence of decreasing capacity of the mercury/solution interface the slope of the almost linear central part of the curve decreases with each addition of the substance. From this decrease the capacity of the electrode can be estimated: at concentration  $5 \cdot 10^{-4}$  mol l<sup>-1</sup> BP in 0.1M phosphate buffer of pH 6.8 the integral capacity corresponds to 55% of the value in pure buffer solution. The curves recorded with varying BP concentration intersect in one point indicating the potential of maximum adsorption near  $-0.5$  V. The effect of adsorption of BP persists on the

polarographic curves up to the positive potential limit due to the electrolytic dissolution of mercury.

In acid solutions, according to pH, one or two protons attach themselves to the nitrogen atoms of the BP molecule, the  $pK_A$  values being 4.8 and 2.7 respectively<sup>15</sup>. When added into solution of a strong acid the molecule forms a doubly charged cation and its effect upon the charging current is essentially different from what was described above: on addition of BP there appears a drawn-out increase of cathodic current over some 200 mV up to the foot of the reduction wave. With further additions of BP this increase grows gradually less and less until a limit is reached, with drop-time of about 4 s, at the concentration of  $5 \cdot 10^{-5} \text{ mol l}^{-1}$ . This concentration dependence indicates that the phenomenon is connected with covering of the surface, but the capacity of the electrode does not appear to be changed in the usual way — it seems as if on adsorption of the doubly protonated BP the capacity increases rather than decreases. The two positive charges at the ends of the long molecule have obviously the tendency to make the molecule approach the negatively charged electrode in an orientation parallel to the surface and thus enable the  $\pi$  electrons of the aromatic rings to interact with the electrons of the metal. It has been known<sup>16</sup> that molecules in  $\pi$  interaction with the surface of mercury electrode do not lower its capacity; however, this interaction is usually limited to a positively charged or uncharged surface. In order to obtain a more precise picture about the different behaviour of BP in the interface of mercury with neutral and acid solutions the data from electrocapillary measurements must be consulted.

### *Electrocapillary Measurements*

From electrocapillary curves obtained with various solutions it turned out that the results in neutral and alkaline media are qualitatively and quantitatively similar and that they differ basically from those obtained in acidic media. Here we present experimental data gained in 0.1M solutions of  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ .

Two parallel sets of electrocapillary curves were obtained with 0.1M solutions of  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  containing BP in concentrations from  $5 \cdot 10^{-6}$  to  $2 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ . The drop-time varied between 56 and 60 s with the average error of  $\pm 0.001$  s when measured at constant potential; when the whole electrocapillary curve was repeatedly measured the reproducibility of drop-time was  $\pm 0.02$  s. The adsorption from more dilute solutions starting by  $2 \cdot 10^{-6} \text{ mol l}^{-1}$  was measured with drop-time around 90 s; the set of the curves yields results overlapping with those obtained with 60 s drop-time, which is a proof of reversibility of the BP adsorption. In neutral solution BP shows relatively strong adsorption without affecting the position of the electrocapillary maximum; in acid solution the adsorption is weaker and the maximum shifts in the direction of positive potentials with increasing BP concentration. The detailed results of electrocapillary measurements in the two media are tabulated

in Tables I and II in terms of interfacial tension  $\gamma$  expressed in  $\text{mN m}^{-1}$  after taking  $\gamma_0$  at the point of zero charge in  $0.1\text{M H}_2\text{SO}_4$  equal  $426.4 \text{ mN m}^{-1}$  (*cf.*<sup>17</sup>).

TABLE I

Equilibrium interfacial tension of Hg in aqueous solution of BP in  $0.1\text{M Na}_2\text{SO}_4$  ( $\text{mN m}^{-1}$ )

$-E$ V vs SCE	Concentration of BP, $\text{mol l}^{-1}$							
	0	$2 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-4}$
0.150	411.0	410.3	410.0	409.4	408.1	404.8	400.5	395.4
0.200	411.0	415.2	414.6	413.6	412.0	408.8	405.1	401.4
0.250	420.0	418.6	417.8	416.7	415.0	411.9	408.8	405.7
0.300	422.9	421.1	420.1	418.9	417.1	413.9	411.2	408.3
0.350	424.8	422.9	421.7	420.3	418.4	415.1	412.5	409.8
0.400	425.9	423.8	422.6	421.0	419.1	415.7	412.9	410.5
0.450	426.4	424.0	422.9	421.2	419.4	415.2	413.2	410.6
0.500	426.2	423.7	422.6	421.1	419.1	415.6	412.9	410.1
0.550	425.4	422.9	421.8	420.4	418.4	414.8	412.2	409.6
0.600	424.0	421.6	420.4	419.0	417.0	413.6	411.1	408.5
0.650	421.9	419.6	418.5	417.2	415.3	412.0	409.6	407.1
0.700	419.5	417.2	416.2	414.9	413.0	410.1	407.6	405.4

TABLE II

Equilibrium interfacial tension of Hg in aqueous solution of BP in  $0.1\text{M H}_2\text{SO}_4$  ( $\text{mN m}^{-1}$ )

$-E$ V vs SCE	Concentration of BP, $\text{mol l}^{-1}$						
	0	$5 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-4}$
0.100	401.5	401.0	400.8	400.5	400.1	398.1	393.9
0.150	407.6	—	—	—	406.3	404.9	401.6
0.200	413.0	412.7	412.4	411.9	411.6	410.9	410.0
0.250	417.5	—	—	—	416.6	415.9	415.1
0.300	421.0	420.7	420.5	420.4	420.1	419.8	419.3
0.350	423.6	—	—	—	423.0	422.6	422.1
0.400	425.3	425.2	425.0	424.9	424.6	424.3	423.8
0.450	426.2	426.05	425.9	425.6	425.4	424.9	424.3
0.500	426.4	426.2	426.0	425.6	425.3	424.6	423.8
0.550	425.9	425.6	425.2	424.8	424.2	423.2	422.4
0.600	424.8	424.0	423.5	422.9	421.9	420.6	419.7
0.650	423.1	412.3	420.4	419.5	418.8	416.6	415.4

The surface pressure  $p_s = \gamma_0 - \gamma$ , *i.e.*, the difference between the interfacial tension in the pure supporting electrolyte  $\gamma_0$  and in the given solution  $\gamma$ , demonstrates the strikingly different behaviour of BP in the two media. While in neutral solution the surface pressure passes through a maximum, in acid solution it passes through a minimum and increases strongly in the negative direction. The increase of the surface pressure near the SCE potential which occurs at higher BP concentrations in both neutral and acid media can be explained by a gradual transition from a non-localized to a localized interaction due to the tendency of BP towards bonding as a ligand with mercury atoms. As there is no d.c. polarographic anodic wave in the region of positive potentials, the interaction obviously does not enhance the dissolution of mercury. The increase of  $p_s$  with increasing negative potential in acid solutions begins at the positive side of the electrocapillary maximum and continues over into the potential region of electroreduction. For its interpretation further results of the electrocapillary measurements have to be considered.

Figs 1 and 2 show the equilibrium charge density – potential dependences obtained by graphical derivation of the electrocapillary curves. They give an exact picture of what has been qualitatively indicated by the polarographic curves of the

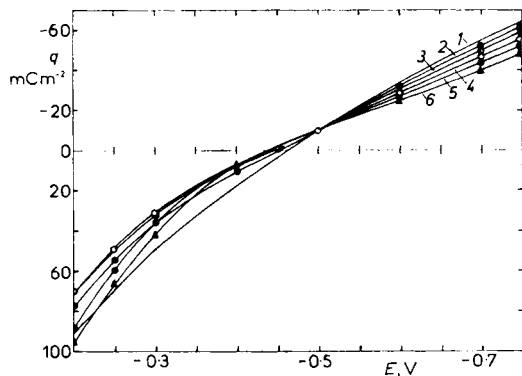


FIG. 1

Dependence of the equilibrium charge density  $q$  on potential in  $0.1\text{M Na}_2\text{SO}_4$ . Concentration of BP ( $\text{mol l}^{-1}$ ): 1 0; 2  $5 \cdot 10^{-6}$ ; 3  $2 \cdot 10^{-5}$ ; 4  $5 \cdot 10^{-5}$ ; 5  $1 \cdot 10^{-4}$ ; 6  $2 \cdot 10^{-4}$

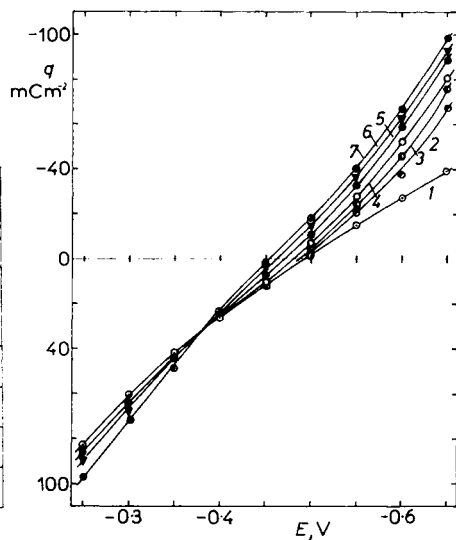


FIG. 2

Dependence of the equilibrium charge density  $q$  on potential in  $0.1\text{M H}_2\text{SO}_4$ . Concentration of PB ( $\text{mol l}^{-1}$ ): 1 0; 2  $5 \cdot 10^{-6}$ ; 3  $1 \cdot 10^{-5}$ ; 4  $2 \cdot 10^{-5}$ ; 5  $5 \cdot 10^{-5}$ ; 6  $1 \cdot 10^{-4}$ ; 7  $2 \cdot 10^{-4}$

charging current: while in neutral solution the increase of BP concentration causes a decrease of negative charge density at the negatively charged electrode, in acid solutions the negative charge density increases with each addition of BP. The doubly protonated BP in adsorbed state does not behave as a dielectric in the condenser of the electrode double layer; it appears that in course of reversible adsorption the contact of the aromatic ion with the metal occurring under  $\pi$  interaction is accompanied by an association of negative charge from the metal with BP. This association is possible, as due to the field of the short-range interaction the local charge density and hence the electric potential at the place of contact on the metallic surface are different from the values at the uncovered surface. After the time of contact has elapsed the BP cation desorbs, the  $\pi$  interaction is interrupted and the charge in the metal is set free again. This kind of surface charge transfer which does not affect the adsorption equilibrium or the concentration gradient at the interface goes gradually over with increasing negative potential into the normal electroreduction process.

From the set of electrocapillary curves for a series of concentrations we plotted a set of  $\gamma - \ln c$  curves for a series of constant values of  $E$ . By graphical derivation of the latter we obtained the values of surface excess  $\Gamma$  according to the Gibbs-Lippmann formula  $\Gamma = (-1/RT)(\partial\gamma/\partial \ln c)_E$ . In Figs 3 and 4 the dependence of  $\Gamma$  on  $E$  is shown for the neutral and acid solution and in Fig. 5 the  $\Gamma - c$  curves, *i.e.*, the adsorption isotherms, are compared for both solutions for the potential region of the electrocapillary maximum. The  $\Gamma - c$  data when plotted in the  $c/\Gamma$  vs  $c$  coordinates to test the validity of the Langmuir isotherm give straight lines: in the neutral solution in the range between  $-0.2$  and  $-0.7$  V to 80% of the total coverage, in the acidic solution between  $-0.3$  and  $-0.45$  V to 50% and between  $-0.5$  and

TABLE III

Data of the linearized Langmuir adsorption isotherm obtained from electrocapillary curves measured in solutions of BP

$E$ V vs SCE	$\Gamma_m$ $\text{mol m}^{-2}$	$1/\Gamma_m$ $\text{m}^2 \text{mol}^{-1}$	$\beta$ $\text{m}^3 \text{mol}^{-1}$	$\Gamma_m$ $\text{mol m}^{-2}$	$1/\Gamma_m$ $\text{m}^2 \text{mol}^{-1}$	$\beta$ $\text{m}^3 \text{mol}^{-1}$
	0.1M Na <sub>2</sub> SO <sub>4</sub>			0.1M H <sub>2</sub> SO <sub>4</sub>		
0.300	$1.96 \cdot 10^{-6}$	$0.51 \cdot 10^6$	$0.86 \cdot 10^2$	$0.23 \cdot 10^{-6}$	$4.27 \cdot 10^6$	$0.39 \cdot 10^2$
0.400	$1.81 \cdot 10^{-6}$	$0.55 \cdot 10^6$	$1.35 \cdot 10^2$	$0.23 \cdot 10^{-6}$	$4.29 \cdot 10^6$	$0.36 \cdot 10^2$
0.450				$0.49 \cdot 10^{-6}$	$2.05 \cdot 10^6$	$0.20 \cdot 10^2$
0.500	$1.81 \cdot 10^{-6}$	$0.55 \cdot 10^6$	$1.41 \cdot 10^2$	$0.57 \cdot 10^{-6}$	$1.76 \cdot 10^6$	$0.26 \cdot 10^2$
0.550				$0.66 \cdot 10^{-6}$	$1.51 \cdot 10^6$	$0.39 \cdot 10^2$
0.600	$1.80 \cdot 10^{-6}$	$0.55 \cdot 10^6$	$1.18 \cdot 10^2$	$0.75 \cdot 10^{-6}$	$1.33 \cdot 10^6$	$0.63 \cdot 10^2$

-0.6 V to 80% of the total coverage. The results of analysis of these plots are presented in Table I. They confirm that BP in neutral solutions is relatively strongly adsorbed: the Langmuir adsorption coefficient  $\beta = 1.41 \cdot 10^2 \text{ m}^3 \text{ mol}^{-1}$  at the

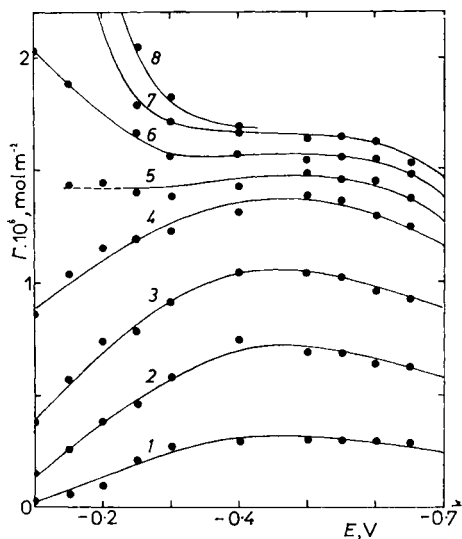


FIG. 3

Dependence of the surface excess  $\Gamma$  on potential in 0.1M  $\text{Na}_2\text{SO}_4$ . Concentration of BP ( $\text{mol l}^{-1}$ ): 1  $2 \cdot 10^{-6}$ ; 2  $5 \cdot 10^{-6}$ ; 3  $1 \cdot 10^{-5}$ ; 4  $2 \cdot 10^{-5}$ ; 5  $3 \cdot 10^{-5}$ ; 6  $5 \cdot 10^{-5}$ ; 7  $1 \cdot 10^{-4}$ ; 8  $2 \cdot 10^{-4}$

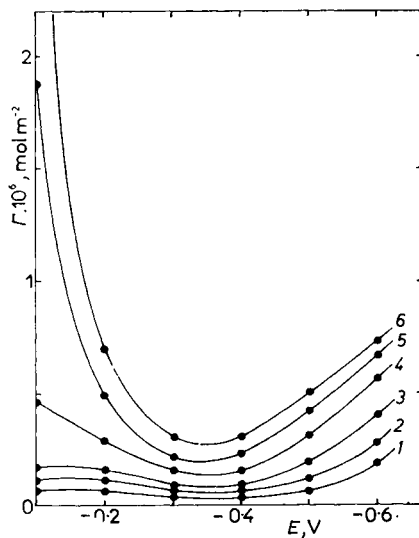


FIG. 4

Dependence of the surface excess  $\Gamma$  on potential in 0.1M  $\text{H}_2\text{SO}_4$ . Concentration of BP ( $\text{mol l}^{-1}$ ): 1  $5 \cdot 10^{-6}$ ; 2  $1 \cdot 10^{-5}$ ; 3  $2 \cdot 10^{-5}$ ; 4  $5 \cdot 10^{-5}$ ; 5  $1 \cdot 10^{-4}$ ; 6  $2 \cdot 10^{-4}$

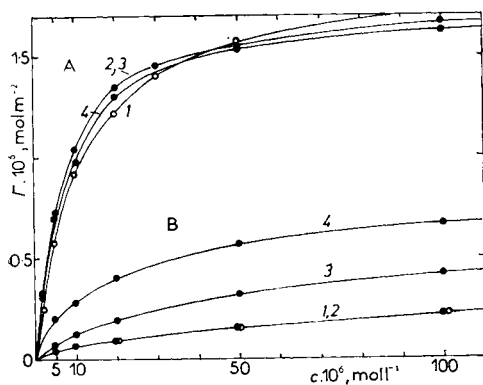


FIG. 5

Dependence of the surface excess  $\Gamma$  on concentration of BP at: 1 -0.3; 2 -0.4; 3 -0.5; 4 -0.6 V (SCE); A in 0.1M  $\text{Na}_2\text{SO}_4$ ; B in 0.1M  $\text{H}_2\text{SO}_4$

potential of maximum adsorption ( $-0.50$  V) when its molecule occupies the area of about  $0.92$  nm<sup>2</sup> at complete coverage. This value represents the area requirement by the dynamic process of reversible adsorption equilibrium involving partial desolvation of the adsorbing and solvation of the desorbing species, which is naturally considerably bigger than the area given by the actual dimensions of the molecule. In acid solutions at the potential of minimum adsorption ( $-0.36$  V)  $\beta = 0.38$ .  $\cdot 10^2$  m<sup>3</sup> mol<sup>-1</sup> and the doubly charged cation in adsorbed state occupies about  $7.10$  nm<sup>2</sup> at complete coverage. This large value is probably due to mutual electrostatic repulsion and to solvation in the adsorption/desorption process. With increasing negative potential this value gradually decreases and the adsorption coefficient increases, presumably due to the effect of the surface charge transfer which reduces the charge on the adsorbed ion. However, at  $-0.50$  V the area occupied by the cation is still more than 3 times greater than that occupied by the neutral molecule. This reflects the difference in approach of the two forms of BP to the electrode: the dication tends to contact the metal with the aromatic rings parallel to the surface enabling thereby the  $\pi$ -interaction.

The different nature of the interfacial behaviour of BP in neutral and in acid solutions is clearly demonstrated also by the dependence of the equilibrium charge density  $q$  on the surface excess  $\Gamma$  (Figs 6 and 7): in neutral solution an increasing adsorption of BP leads to a decrease of the negative charge density on the electrode due to decreasing capacity; in acidic solution, on the other hand, the negative charge density on the electrode increases linearly with  $\Gamma$  due to the surface charge transfer process.

Similar interfacial behaviour to that of the doubly protonated BP has been observed also with methylviologen and other bisquaternary salts derived from bipyridyls; the interactions of methylviologen with mercury are the subject of our following communication<sup>18</sup>. The adsorption of BP on mercury is the reason of higher sensitivity of its analytical determination by electroanalytical techniques; the knowledge of the adsorption parameters is prerequisite for optimization of the conditions for an analytical procedure, as is demonstrated by the case of BP in a separate paper<sup>19</sup>.

The results of our measurements in neutral solutions differ to a certain extent from those obtained by the other authors<sup>9,10</sup>. This can be due partly to the difference in the basic electrolytes ( $0.1$  M Na<sub>2</sub>SO<sub>4</sub> and  $2$  M KNO<sub>3</sub>), partly to the difference in the experimental techniques.

#### Interactions at the Limit of Electroreduction: The Adsorption Prewave

The electroreduction of BP in aqueous solutions of pH up to about 9 begins<sup>7,20,21</sup> by the uptake of one electron and formation, after combining with the due protons, of the cation radical H<sub>2</sub>BP<sup>+</sup>; in solutions of higher pH the molecule of BP takes up two electrons in one complex process. With increasing concentration of BP we can follow on the curves the development of the characteristic adsorption prewave<sup>20,22</sup>



studied in particular by Volke and Volková<sup>7</sup> (Fig. 8). In acidic solutions this prewave develops on top of the above described smaller and more positive primary prewave due to the surface charge transfer which starts appearing from the lowest concentrations of BP. In various 0.1M supporting electrolytes and with drop-time of about 3 s the prewave attains its limiting height at BP concentration of  $2 \cdot 10^{-4} \text{ mol l}^{-1}$ . At higher concentrations the rising part of the prewave acquires the typical discontinuous shape indicative of a fast potential-independent process.

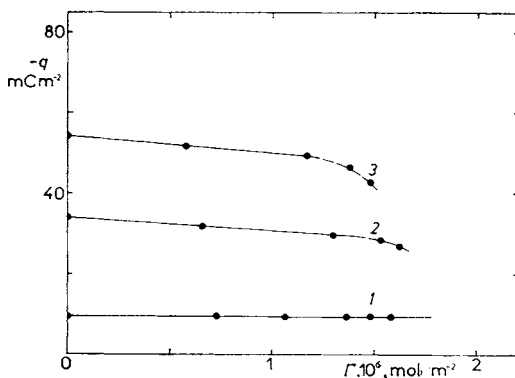


FIG. 6

Dependence of the equilibrium charge density  $q$  on the surface excess  $\Gamma$  in 0.1M  $\text{Na}_2\text{SO}_4$  at potentials: 1 -0.50; 2 -0.60; 3 -0.70 V (SCE)

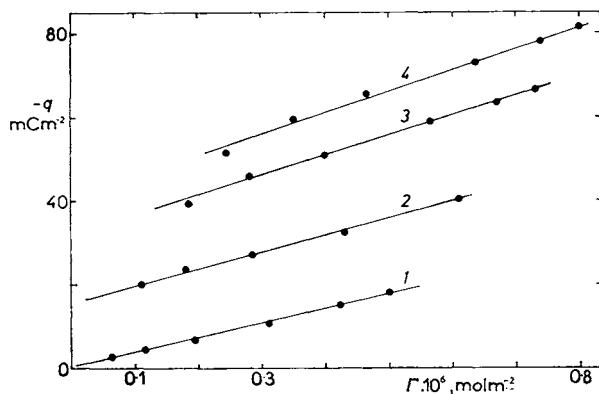


FIG. 7

Dependence of the equilibrium charge density  $q$  on the surface excess  $\Gamma$  in 0.1M  $\text{H}_2\text{SO}_4$  at potentials: 1 -0.50; 2 -0.55; 3 -0.60; 4 -0.625 V (SCE)

According to the properties described in the literature<sup>7,22</sup> as well as to the results reported below this prewave is due to formation at the surface of the electrode of a layer of crystals of a sparingly soluble salt of the radical cation. The low solubility of some salts of the BP radical cation has been known since the radical was prepared for the first time<sup>23</sup>; similar property of various viologen radical cations was thoroughly investigated and practically utilized in display techniques<sup>3,24,25</sup>. The crystallization of salts of various species on mercury surface, among others also of the BP radical, has been studied by Gierst and coworkers<sup>25</sup>.

The radical cation itself is reversibly adsorbed at the electrode; in presence of sufficient concentration of certain anions in the solution a structure near to that of the crystalline lattice is formed in adsorbed state and the salt deposits on the surface as a new phase. The orientation of the adsorbed radical cations and their polarization in the electric field at the electrode favour the crystallization process. The area occupied by one molecule of the salt of the BP radical cation in adsorbed state as calculated<sup>7</sup> from the adsorption prewave is considerably smaller than the  $\Gamma_m$  value of BP obtained from electrocapillary measurements — this is consistent with the static nature of the adsorbed layer; in this case it is justified to compare the area with molecular dimensions of the crystal. From the differential capacity — potential curves of mercury in BP solution<sup>8,10</sup> it appears that the adsorption of the layer of the insoluble salt is marked by a strong lowering of the capacity. Unlike the dynamic system of BP equilibrium adsorption the compact layer of the BP radical cation salt represents a barrier blocking electron transfer processes<sup>7</sup>.

The separation of the prewave from the main wave and its shift towards less negative potentials is due to free energy of the process following the reversible electrode reaction proper:

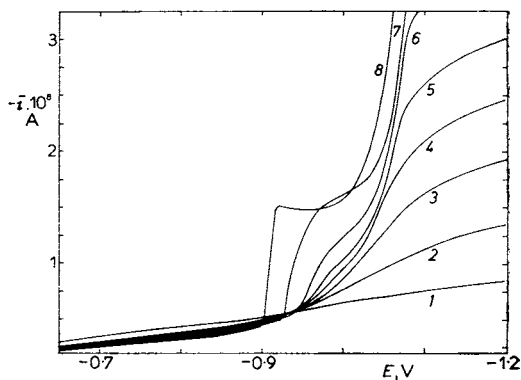
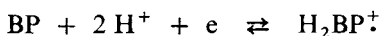
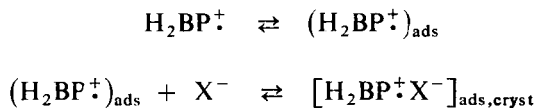


FIG. 8

Formation of the adsorption prewave in d.c. polarographic reduction of BP in 0.1M borate buffer pH 8.0. Concentration of BP ( $\text{mol l}^{-1}$ ): 1 0; 2  $2 \cdot 10^{-5}$ ; 3  $4 \cdot 10^{-5}$ ; 4  $6 \cdot 10^{-5}$ ; 5  $8 \cdot 10^{-5}$ ; 6  $1 \cdot 10^{-4}$ ; 7  $2 \cdot 10^{-4}$ ; 8  $5 \cdot 10^{-4}$



The extent of the shift is determined by the concentrations of BP and of the anion  $\text{X}^-$  and by insolubility of the salt as well as by the free energy of adsorption of the crystalline layer at the electrode. The situation is similar to that of the prewave accompanying anodic dissolution of mercury in presence of various compounds forming insoluble salts with mercury ions<sup>27</sup>. In the potential range of the prewave the DME covered by the layer of an insoluble salt behaves as an electrode of the second kind.

Particularly prominent is the adsorption prewave in phosphate buffer, as shown in Fig. 9. From the potential difference between the prewave and the main wave compared in several 0.1M basic solutions we can conclude that, providing the adsorption energy of various salts does not depend much on the anion, the solubility of the salts of the BP radical cation decreases in the sequence: acetate, perchlorate, borate, dihydrogen phosphate. By adding a higher concentration of sodium perchlorate into a phosphate solution we attain a lower solubility of the BP radical cation, as the shift of the adsorption prewave in Fig. 9 indicates.

The prewave appears also with solutions of pH between 8 and 9 where on the curves there is only one 2-electron reduction wave. This shows that even in those conditions the radical cation is generated at the electrode in sufficient concentration that the formation of its salt in adsorbed state can take place. When the pH of the solution further approaches the  $\text{p}K_{\text{A}}$  values of the radical cation<sup>28</sup>, 10.4, the  $E_{1/2}$  of BP reduction has shifted to negative potentials to that extent that BP radical cation is no more adsorbed; in the reaction mechanism of the electroreduction another path has then prevailed in which the radical cation does not appear any more.

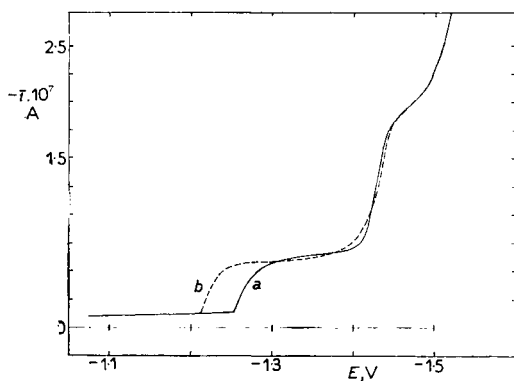


FIG. 9  
D.c. polarographic first reduction wave of BP with the adsorption prewave: a 2.  $\cdot 10^{-4}$  mol l<sup>-1</sup> BP in 0.1M phosphate buffer pH 6.8; b + 1.0M NaClO<sub>4</sub>

## REFERENCES

1. Michaelis L., Hill E. S.: *J. Gen. Physiol.* **16**, 859 (1933).
2. Summers L. A.: *The Bipyridinium Herbicides*. Academic Press, New York 1980.
3. Bird C. L., Kuhn A. T.: *Chem. Soc. Rev.* **10**, 49 (1981).
4. Ebbesen T. W., Ferraudi G.: *J. Phys. Chem.* **87**, 3717 (1983).
5. Heyrovský M.: *J. Chem. Soc., Chem. Commun.* **1983**, 1137.
6. Heyrovský M.: *J. Chem. Soc., Faraday Trans. 1*, **82**, 585 (1986).
7. Volke J., Volková V.: *This Journal* **37**, 3686 (1972).
8. Mambetkaziev E. A., Shaldybaeva A. M., Statsiuk V. N., Zhdanov S. I.: *Elektrokhimiya* **11**, 1750 (1975).
9. Akhmetov N. K., Kaganovich R. I., Mambetkaziev E. A., Damaskin B. B.: *Elektrokhimiya* **13**, 280 (1977).
10. Akhmetov N. K., Kaganovich R. I., Damaskin B. B., Mambetkaziev E. A.: *Elektrokhimiya* **14**, 1761 (1978).
11. Novotný L., Smoler I.: *J. Electroanal. Chem.* **146**, 183 (1983).
12. Novotný L., Smoler I., Kůta J.: *This Journal* **48**, 964 (1983).
13. Novotný L.: *J. Electroanal. Chem.*, in press.
14. Novotný L., Herout M.: *Czech. Appl. No. PV 8728--9*, Prague (1984).
15. Ashton L. A., Bullock J. I., Simpson P. W. G.: *J. Chem. Soc., Faraday Trans. 1*, **78**, 1961 (1982).
16. Damaskin B. B., Petrii O. A., Batrakov V. V.: *Adsorption of Organic Compounds on Electrodes*. Plenum Press, New York 1971.
17. Damaskin B. B., Petrii O. A.: *Vvedenie v elektrokhimicheskuyu kinetiku*. Vysshaya shkola, Moscow 1975.
18. Heyrovský M., Novotný L.: *This Journal*, in press.
19. Novotný L., Andriewski R., Krumbein A., Kalvoda R.: unpublished results.
20. Falqui M. T., Secci M.: *An. Chim. (Roma)* **48**, 1168 (1958).
21. Roullier L., Laviron E.: *Electrochim. Acta* **22**, 669 (1977).
22. Volke J. in the book: *Die Polarographie in der Chemotherapie, Biochemie und Biologie* (H. Berg, Ed.), p. 70. Akademie-Verlag, Berlin 1964.
23. Dimroth O., Frister F.: *Chem. Ber.* **55**, 3693 (1922).
24. van Dam H. T., Ponjé J. J.: *J. Electrochem. Soc.* **121**, 1555 (1974).
25. Bookbinder D. C., Wrighton M. S.: *J. Electrochem. Soc.* **130**, 1080 (1983).
26. Thomas F. G.: *lecture given at the J. Heyrovský Institute*, **14. 5. 1984**.
27. Heyrovský J., Kůta J.: *Principles of Polarography*, p. 167. Academia, Prague and Academic Press, London 1965.
28. Rao P. S., Hayon E.: *Anal. Chem.* **48**, 564 (1976).