STUDIES ON SEMICONDUCTIVE NATURE OF BRDIČKA CURRENT

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Bovine serum or egg white shows a peak wave (so-called presodium wave) at c. $-1\cdot8$ V (s.c.e.) in NH_4Cl or LiCl solution. This wave is enhanced by adding iodine, o-chloranil or cobalt ions and depressed by hydroxyl ions. If ammonium hydroxide and Co(II) ions are added to the solution, a double wave appears for protein at c. $-1\cdot4 \sim -1\cdot6$ V or a single wave for cysteine at c. $-1\cdot6$ V; the presodium wave is depressed. These phenomena correspond to the conductivity effect of organic semiconductor, showing that the c. $-1\cdot4$ V is a n-type, the c. $-1\cdot6$ V wave is an amphoteric type, and the presodium wave (c. $-1\cdot8$ V wave) is a p-type wave. Such a n-, amphoteric or p-type current is caused by exchange of electrons and/or holes between mercury electrode (with or without Co) and its adsorbate at a proper cathodic potential. The latter types of the waves are partly modified by the effect of electron donors or acceptors, which change their height. They are simulated by an inorganic semiconductor, e.g., cobalt sulfide, by the suspension or press-on method as formerly reported. Consequently a hybridized electrode surface system composed of Hg (with or without Co)/solution and Hg (with or without Co)/semiconductore/solution is considered to be closely related to the Brdička current. Some results of studies on the relation between polarographic behaviour and semiconductor characteristics are reported.

In our studies[1,2] of the mechanism of the Brdička catalytic hydrogen waves of proteins[3] we also used hydrogen sulfide instead of protein and found strong excitation of current in the potential region of the protein wave. Analogous effect was observed when powdered cobalt sulfide suspended in the solution of the supporting electrolyte by means of magnetic stirrer was used[4]. Application of this "suspension method" on more than 15 inorganic semiconductor materials manifested some regularities between each decomposition or peak potential and corresponding energy gap or work function[5-7].

Another method of examining solid state semiconductors which we used in our studies was based on mechanical contact of hanging mercury drop with the pressed piece of the sample. It showed an analogous current which, however, did not decrease at potentials at which the current measured by other methods decreased. In this "press-on method"[8,9], plastic film with an Al_2O_3 layer for thin layer chromatography was cut into $0\cdot7 \times 5$ cm strips, powdered or irregularly formed sample was located on one end of such a strip and the other end was held with a protractor which served for control of press-on angle against D.M.E.

Recently, we found that many kinds of biological materials and some plastics also show similar phenomena when the "suspension" or "press-on" methods are used. In this connection, we decided to elucidate also the Brdička effect from the point of view of the semiconductor, i.e., protein adsorbed on the surface of D.M.E.,

which is in mechanical contact with an electrode surface. Therefore, in the present paper, semiconductive characteristics of the Brdička current are discussed.

EXPERIMENTAL

Yanagimoto P-8 Polarograph and P-1000 type Voltammetric Analyzer were used for d.c. polarography. Yanagimoto PE-20 Polaronsion was used for Ševčík type oscillographic polarography as supplemental work.

Bovine serum prepared by Institute of Microbiology, Osaka University, and egg white of a hen or of a quail were used as protein representatives. Three types of sample preparation were used; they are summarized in Table I.

0·1 ml of each sample prepared according to the Table I was then mixed with 4·9 ml of one of the following base solutions; No. 1 of these solutions is customarily used for an ordinary Brdička reaction: (1) 0·1 F NH_4Cl, 0·1 F NH_4OH, 0·001 F $CoCl_2$; (2) 0·1 F NH_4Cl; (3) 0·1 FLiCl.

Egg shell with membrane was rinsed with water after the contents were removed. About 1 cm^2 of the air-dried shell was then dipped in 5 ml of the base solution and shaken several times. The rinsings obtained were suitable for native protein tests.

0·05 ml of alcoholic solution of iodine of $8·6 . 10^{-3}$ F and of saturated water solution of ortho-chloranil (o-CA)[10] were added to 2·5 or 5 ml of an electrolytic solution for testing whether the depolarizer involved shows a n-type or a p-type semiconductive nature in the electrode reaction.

All reagents mentioned above were of chemically pure grade and products of Nakarai Co. except o-Ca which was Aldrich Chem. Co. reagent.

For comparison with proteins, two kinds of low molecular weight thiols (LMWT), i.e., 1-cysteine hydrochloric acid (Reagent grade, Nippon Rikagaku Yakuhin Co., ltd.) and 1-cystine (Guaranteed reagent, Kishida Chemicals Co., ltd.), have been chosen.

Judgement of n- or p-type of solid samples was carried out by means of conventional measurement of thermal e.m.f.

RESULTS AND DISCUSSION

Ordinary filtrate reaction of Brdička current is shown as curve a in Fig. 1. At c. −1·25 V vs S.C.E. a cobalt wave is seen. In the region from c. −1·3 to −1·7 V vs S.C.E. there is a double wave, though it is hardly recognizable because of insufficient sensitivity intentionally preset. At the final ascent of current in the curve no "presodium wave" (cf. and Heyrovský Babička[25]) is seen. But upon adding some precipitate, which has been made with sufosalicylic acid (SSA) and separated by filtration from the filtrate mentioned above, all the waves but that of the cobalt are very much enhanced. The presodium wave is clearly seen at c. −1·8 V as shown in Fig. 1, curve b, taken by suspension technique. This kind of strong activity of SSA-precipitate was found by one of the present authors in 1956, but the cause has not been clarified until its semiconductive nature was understood.

Kuik[11] pointed out the three kinds of peaks (I, II and III) on the cysteine wave in Brdička solution of cysteine–nickel system. These peaks appear approximately

in the region from about -1.5 to -1.9 V *vs* s.c.e. But the reason for the origin of these peaks was not explicitly stated. The variations of the peaks with the experimental conditions suggest that the peaks *I* and *II* correspond to our *c.* -1.6 V wave

TABLE I

Sample preparation. Take and add from the left to the right. Each figure is in ml. After adding KOH let stand 30 minutes. SSA is the abbreviation of sulfosalicylic acid

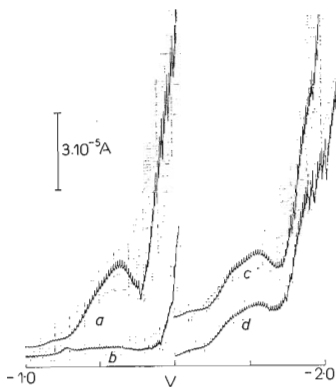| Protein	Protein	Water	1F-KOH	20% SSA	Water
Native	0·4	1·4	—	—	—
Denatured	0·4	0·4	0·2	—	0·8
Filtrate	0·4	0·4	0·2	0·8	(take filtrate)

FIG. 1

Bovine serum in base solution (*I*); ammonia-–ammonium chloride solution with Co^{2+}. *a* Filtrate reaction; *b* solution *a* with *c.* 1/10 of original SSA ppt., by a suspension method; *c* native serum reaction; *d* solution *c* with 0·002% tween 40
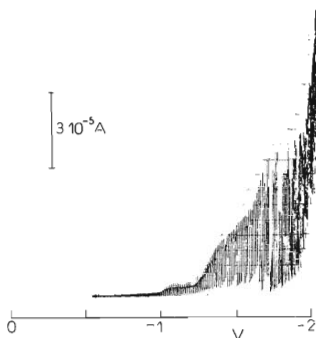

FIG. 2

Boiled quail egg white in base solution (*I*) by the press-on method; ammonia-ammonium chloride solution with Co^{2+}

and the peak *III* to our *c*. −1·8 V wave, which we recognized experimentally with cysteine– or cystine–cobalt system.

In Fig. 1 curve *c*, a curve similar to that of SSA-precipitate suspension (curve *b*) is seen by native serum reaction. When two drops of 0·1% tween-40 are added to 5 ml of the sample solution, a lower wave which resembles more closely the double wave than before adding tween is seen as curve *d*. It suggests that the surface active substance inhibits to some extent the intensity of adsorption of protein.

Polarogram in Fig. 2 was recorded with boiled quail egg white in base solution (*1*) using the press-on method. This case indicates the strongest adsorption. The form of the curve is considered homologous with that of curves *b* or *c* in Fig. 1. However, the current rise is not so steep and there is no decrease of the current in the whole potential region tested, what indicates the intimate contact between mercury and the sample. As a matter of fact, the native serum reaction without any surface active substance usually exhibits a comparatively strong and steadily ascending current as in Fig. 2.

The potential of the Co^{II} to Co^0 reduction wave is also susceptible to surface adsorption of a protein on the mercury electrode. Curve *a* in Fig. 1 shows cobalt wave with a small maximum at the potential of −1·25 V close to the double wave; curve *b* in this figure has a cobalt wave in a normal form (*i.e.*, without the maximum and at somewhat more positive potentials (−1·12 V). Finally, in Fig. 2 this wave lies at still more positive potentials (−1·03 V). This potential shift is thought to be a consequence of the varying adsorptive intensities concerning a protein. Adsorption of this kind seems to lower the activation energy of cobalt reduction, while tween-40 has no effect on it.

In simple case, the adsorbate is composed of a protein or a LMWT which is adsorbed on mercury presumably by coordinative association between mercury and sulfur, nitrogen, or oxygen in an organic molecule. When cobalt or nickel ions are simultaneously present the adsorbate could be in the form of an organic complex of the metal. This kind of complex is formed in Brdička solution, as has been widely thought, and should have a cationic form. But protein usually bears an overall negative charge under the Brdička conditions, so that it may be repelled from the cathode. However, there may be positive charges in the molecule due to intramolecular zwitter ionic localization of electrons as is usually seen in a semiconductive organic compound. Such positive ends of the complex molecules can be electrostatically attracted to the cathode and form the adsorbate composed of regularly oriented molecules which are able to display semiconductive nature. This view is thought to be applicable both to the macromolecular protein complex (as an intra-molecular semiconductor) and the LMWT complex (as an inter-molecular semiconductor[10−12]).

The Brdička catalytic hydrogen current produced in alkaline solution has been explained by many authors as a consequence of the fact that the SH groups of the

ligand must be dissociated in order to be able to combine with cobalt. If the complex is produced in the bulk of the solution, the dissociated hydrogen ions must be instantly neutralized with ammonia and can not be transfered up to the electrode surface. To overcome this contradiction one must expect the electrode process involving the complex formation in the vicinity of the electrode surface for hydrogen production, and the following hydrogen uptake done by an unthinkable way from the solution for continuation of hydrogen evolution. The semiconductive conception introduced in the present paper elucidates this problem as follows: The adsorbate consists of a metal–protein or a metal–cysteine complex. The complex adsorbate has at least one coordination bond between the metal atom and the sulfur atom originated from the SH group, being in the state of the resonance hybrid molecules containing —M—S̈—C— and —M—SH—C—. Analogously, a combination —NH₂ and —NH₃⁺
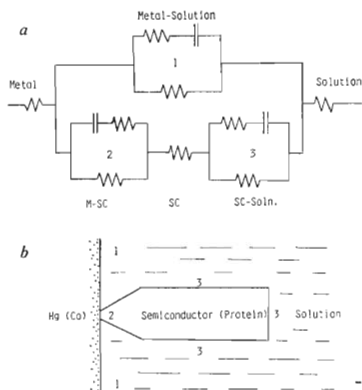

FIG. 3

Schematic illustration of the hybrid interfaces among mercury electrode, semiconductor and electrolytic solution. a equivalent circuit, b conceptual picture. 1 Solution-metal interface; 2 metal–semiconductor interface; 3 semiconductor–solution interface
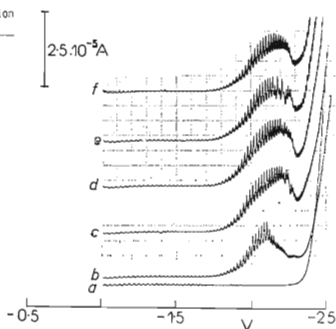
FIG. 4

Native hen egg white (the rinsings of membrane) in base solution (3); lithium chloride solution. a Base solution; b solution a with egg white; c solution b with platinum dust (1 mg/2·5 ml); d solution b with RuO_2 powder (1 mg/2·5 ml); e solution b with iodine ($1 . 10^{-3}$ F I₂); f solution b with o-CA (1 drop/2·5 ml)

has been taken into account[13]. From the cathodic surface of the electrode electrons are fed to the semiconductor, either directly or *via* inter-molecular transference into the molecule. After the electrones overcome the interfacial charge barrier they are transfered through intra-molecular route to the hydrogen atoms of the SH groups and reduce then to gas. The vacancies of the hydrogen atoms thus produced must be replaced with fresh atoms supplied from the solution in conformity with the mass action law. However, to some extent the SH group can also combine with hydrogen to form H_2S gas which is usually found in small amounts in the electrolytically collected hydrogen gas on the mercury cathode under the Brdička conditions. Hydrogen sulfide gas in also found when an inorganic semiconductor, *e.g.*, powdered CoS or NiS, is used by suspension method[6,26,27]. It suggests that hydrogen atom is near the sulfur atom in an adsorbate molecule.

Returning to the above mentioned analogy between the protein waves taken by means of an ordinary polarographic method, suspension method, and press-on method we have to reconsider the structure of the electrode surface. Each polarogram in Figs 1 and 2 shows the cobalt(II) reduction wave and the final ascent of the current. It means that there is a part of the mercury surface which remains free after the deposition of the adsorbate. The catalytic waves due to the protein are located between the cobalt wave and the final ascent of current. The modes of contact between protein and mercury are different in the above three methods, yet their natures are the same, although intensities of currents are individually different. These waves show characteristics of the kinetic current[1,2,4] as well as of the current due to the semiconductor[5-7]. Consequently, the electrode surface of mercury in contact with protein is an important element of the electrode surface structure necessary to furnish a protein reaction. In this case, any type of contact, *i.e.*, adsorption, hitting or pressing of protein against mercury drop, is similarly active with more or less intensity of current; the schematic picture and corresponding equivalent circuit are shown in Fig. 3*a*. and *b*. This is a hybrid electrode process composed of interfaces of Hg (with or without Co)/soln. and Hg (with or without Co)/semiconductore/soln.

To elucidate the Brdička current from the point of view of the semiconductor it is necessary to determine some solid state properties of the protein or LMWT concerned. Above all, it is important to know whether the sample is of the *n*- or *p*-type. It is well known that an electron donor or acceptor as a dopant increases electric conductivity(dark) of *n*-type or *p*-type semiconductor, respectively, while decrease is subjected to opposite combinations. If this general rule is adequate to a protein or a LMWT current in polarography, it is not only useful to know the *n*- or *p*-type of sample but also to characterize a polarographic kinetic current. Accordingly, it is helpful to support the above assumption of a hybrid electrode process involved in Brdička current.

Protein as a biological organic macromolecule has an energy gap (thermal activa-

tion energy) of *c.* 2·7 eV in dry state[10]. The dried protein (*e.g.*, serum albumin) is usually a *p*-type semiconductor, because its dark conductivity is increasing by a factor 10^6 upon adding *o*-CA which is an electron acceptor[14]. On the contrary, a small quantity of water (electron donor) decreases the conductivity by a factor 10^{-1}. But a large quantity of water[15] makes protein *n*-type and increases the conductivity by a factor 10^5. This kind of transformation is said to be a tendency of biological macromolecules (Brillouin's assumption — 1978)[12]. The test by thermal e.m.f. method reveals that boiled egg white, cobalt sulfide powder, cysteine powder and cystine powder are *p*-types, and with ammonium hydroxide some parts of these substances turn to n-type and/or amphoteric type.

Fig. 4 shows polarograms of native egg white (the rinse of the membrane) in lithium chloride solution. Curve *a* is a blank polarogram of base solution (*3*), lithium chloride. In curve *b*, a peak wave of protein is seen at *c.* −2·2 V *vs* S(LiCl). C.E.. At such a highly negative potential one cannot carry out observation when base solutions (*1*) or (*2*) are used. Curves *c*, *d*, e, and *f* were recorded after adding platinum[16] (less than 1 mg of scratched dust of Pt wire per 2·5 ml electrolytic solution; addition of chloroplatinum ion is also effective), ruthenium dioxide[17] (*c.* 2 mg powder per 2·5 ml), iodine (8·6 . 10^{-4}M alcoholic solution, 0·05 ml I_2 solution per 2·5 ml) and *o*-CA (0·05 ml of saturated water solution per 2·5 ml), respectively. The peak heights are 1·28, 1·21 and 1·10 times greater than that in curve *b*.

Hence, all additives tested enhanced the peak height values. Among them, iodine and *o*-Ca are typical acceptors[12] and generally increase *p*-type activity. This is also the case here. Accordingly we conclude that both ruthenium dioxide and platinum play a role of acceptors in the present case. Therefore, the native protein wave in lithium chloride solution can be classified as a *p*-type polarographic current–voltage curve. Hereupon, the current initially increases as the applied voltage is cathodically increased, but later it becomes decreasing before the final ascent of lithium ion, shown in all curves of Fig. 4, is achieved. It is understood that these currents are caused by exchange of carriers (*i.e.*, electrons and/or holes) between mercury electrode and *p*-type protein which was adsorbed on the electrode surface already at the less negative potentials than those of the catalytic wave. As soon as the applied potential attains the polarization (*c.* −1·7 V) sufficient to surmount the energy barrier of the interface of mercury and space charge surface layer of protein (*p*-type), the carriers begin to move to make the current flow. Such a carrier exchange between D.M.E. and its adsorbate must be one of the categories of the polarographic currents. When cobalt ions are present in the solution, the interface consists of cobalt amalgam[1] and adsorbate. As the work function[18] of cobalt ($\phi = 4\cdot21$ eV) is smaller than that of mercury ($\phi = 4\cdot50$ eV), cobalt deservedly facilitates the electron transfer from the electrode to the adsorbate or inhibits the transfer of holes to promote the cathodic depolarization.

However, the shift of overpotential (difference between Fermi level of the metal

electrode and the free energy of the redox hydrogen system divided by Faraday constant) from that of mercury to that of the amalgam does not affect the activation energy for the electrode process but influences appreciably the carrier concentration of the semiconductor at the interfacial space charge region[19]. This effect is considered to be the main cause of enhancement or depression of current due to the semiconductive adsorbate on D.M.E.. The cause for enhancement of the presodium wave by cobalt described by Jurka[20] can now be easily explained on the basis of the semiconductive nature. Other experiments on the current enhancement effects of nickel[11] ($\phi = 4.32$ eV), zinc[21] ($\phi = 3.40$ eV), thallium[21] ($\phi = 3.84$ eV), and cadmium[21] ($\phi = 4.00$ eV) used instead of cobalt can be interpreted by the same principle. Further, the occurrence of the surface turbulence, to which Stackelberg and coworkers[22] and Březina and Kůtová[21] attributed the enhancement of the catalytic wave by a metallic ion, can be explained considering the semiconductive nature of the electrode process. Generally, metal with lower work function than that of mercury deposits on the surface of mercury electrode which remains free after adsorption of the depolarizer, and makes electron concentration of the adsorbate higher than before to enhance the current at a suitable potential. This process is accompanied by an electrostatical unbalance of charge distribution of the interface resulting in the surface turbulence.

In this connection, the factor which causes the decrease of current in the curves in Fig. 4 must also be considered. Since an alkali metal, *e.g.*, Li, Na, K or perhaps NH_3 is a typical electron donor, it makes a *p*-type current less active. So, the presodium wave has its final form like a plateau or a maximum.

There are other explanations for the maximum shape of the catalytic hydrogen waves in the literature. For example, Mairanovskii[23] proposed theoretical explantion taking into account the desorption process. But we prefer the following interpretation: The distribution functions of electron energy levels in the semiconductor surface and in the redox system of hydrogen in the solution at the interface with the semiconductor are basically expressed by exponential functions. Since the electron exchange at the interface between both phases depends on equipotential overlaps of these functions, the current also results in an exponential distribution[19] along potential axis to form a peak wave of polarographic current voltage curve.

Presodium waves can be seen also in Figs 1, 5 and 6. They are thought to be of the same nature as the waves in Fig. 4, because they are enhanced by iodine (Figs 5 and 6), thus indicating the characteristics of the *p*-type. However, their wave forms are not completely analogous to those in Fig. 4. This is clearly due to the difference in the value of the potential at which the final ascent of current begins. While the first half of the waves in Fig. 4 and in Figs 1, 5 and 6 is very similar, the latter half is different since, in Figs 1, 5 and 6, it is superimposed with large currents due to the reduction of ammonium, potassium or sodium ions. This is the true character of the presodium wave.

In the case of the Brdička double wave, the suppressive effect of iodine or o-CA is seen as shown in Fig. 5, curves c and d, as well as in Fig. 6, indicating that the double wave is n-type which has been converted from original p-type resulting from water effect induced by the addition of ammonium hydroxide[15].

According to Kuik and Basiński[24], the height of cysteine peak $(c. -1\cdot6$ V$)$ in NH_3–NH_4Cl–Ni^{II} system changes with concentration of ammonia and ammonium chloride. This change exhibits an optimum, which these authors could hardly explain by assuming some catalytically most active nickel–cysteine complexes. Our semi-conductive concept works well to elucidate the above behaviour. As mentioned above in the case of the cobalt–protein system, the $c. -1\cdot6$ V wave behaves as a rule as being an intermediate type between the $c. -1\cdot4$ V $(n$-type$)$ and the $c. -1\cdot8$ V $(p$-type$)$ waves,
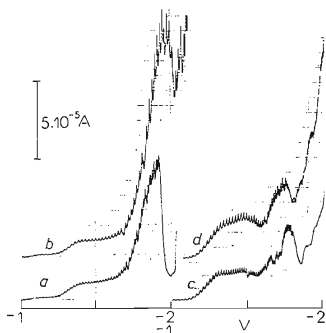

FIG. 5

Hen egg white in base solution (I); ammonia––ammonium chloride solution with Co^{2+}. a Denatured protein reaction; b solution a with iodine $(8 . 10^{-4}$ F $I_2)$; c solution d with iodine $(8 . 10^{-4}$ F $I_2)$ (double wave is depressed by a factor $0\cdot4$, p-type wave is enhanced by $1\cdot27)$; d filtrate reaction
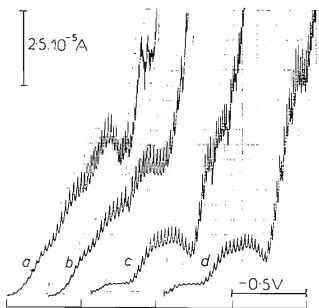
FIG. 6

Double waves of hen egg white (the rinsings of membrane). Each curve starts from $-1\cdot0$ V vs S.C.E. a the wave from Fig. 4, curve b, was converted into the double wave by adding $Co^{(II)}$(resulting conc. $2\cdot38 . 10^{-3}$ F) and ammonia buffer (resulting conc. $0\cdot1$ F NH_3, $0\cdot1$ F NH_4Cl); b solution a with iodine $(1 . 10^{-3}$ F $I_2)$ (double wave is depressed by a factor $0\cdot58$ for the first peak and $0\cdot74$ for the second peak); c filtrate reaction in base solution (I); d solution c with RuO_2 (1 mg//$2\cdot5$ ml)

i.e., the amphoteric type. Nickel behaves similarly to cobalt and cysteine produces usually *c.* −1·6 V amphoteric wave.

Fig. 6, curve *a*, shows the double wave transformed from the native protein curve in lithium chloride for the sake of model experiment of the above assumption. To the solution of the native protein in lithium chloride, cobaltous ion was added in resulting concentration of $2\cdot 38 \cdot 10^{-3}$ F; this brought about an appearance of the cobalt wave and an enhancement of the *p*-type wave at *c.* −1·8 V. To the solution of ammonia–ammonium chloride were added to attain 0·1 F concentrations. Resulting polarogram is shown in curve *a* in Fig. 6. This double wave looks like a cancerous wave because its second peak is higher that the first peak (*n*-type). The reason for this is not clear now but presumably two kinds of constituents are involved, though both of them decreased their currents by iodine as shown in Fig. 6, curve *b*. But the second peak of the double wave is enhanced by further addition of iodine showing that it involves *p*-type other than *n*-type, *i.e.* amphoteric type. Incidentally, pathological meanings on the amphoteric type constituents in a cancerous serum are expected. Curves *c* and *d* are supplementary exhibition of the ruthenium dioxide effect on ordinary filtrate reaction of egg white from egg membrane rinsings.

CONCLUSIONS

1) Powder or fragment of a semiconductor can be studied polarographically by means of the suspension method or the press-on method, respectively. Their homologous activities lead to the general concept of the semiconductor waves. The latter waves involve also the polarographic protein waves including the Brdička currents of proteins and LMWT.

2) Semiconductive *n*-type, amphoteric type and *p*-type polarographic current--voltage curves are found and defined. The first peak of the double wave of the Brdička filtrate reaction belongs to the *n*-type and the second peak is an amphoteric type. The presodium wave belongs to the *p*-type. These three different types of the waves are located at potentials of *c.* −1·4 V, *c.* −1·6 V and *c.* −1·8 V, respectively. They are mutually transformable by proper dopant. Formation of semiconductive surface layer on the D.M.E. is a consequence of adsorption of the semiconductive depolarizer, *i.e.*, protein, LMWT, or their cobalt complexes. The results also suggest interpretation of cancerous polarographic reaction from the point of view of the semiconductive nature of serum constituents.

3) Polarography can contribute to the solid state physics of semiconductors since it can determine electrochemically some physical constants of semiconductors, *e.g.*, Fermi energy, energy gap, carrier densities, minimum energy of conduction band and maximum energy of valence band, *etc.* This is particularly promising in the field of biological macromolecules.

4) Other types of the polarographic maximum waves, catalytic waves and kinetic currents should be re-examined from the point of viw of their semiconductive nature.

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